XXXVII. *On the Condition of certain Elements at the moment of Chemical Change.* *By* BENJAMIN COLLINS BRODIE, *Esq., F.R.S.*

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THE experimental inquiry which I now lay before the Society is so intimately connected with certain theoretical considerations, in which it took its rise, and which are necessary to its right comprehension, that I am unwilling to separate them. These considerations alone can explain why it appeared to me desirable to devote much time and labour to the determination of a simple analytical problem, which it has been open for the last thirty years to any chemist to undertake, but which, although doubtless connected with some of the most curious and obscure phenomena of chemical science, no one has thought it worth his while to enter upon. The reason of this may have been, that from other points of view this inquiry seemed of little importance, or, which is also probable, the question may have been, at various times, partially investigated, and the answer to it thought to be other than what it truly is, because approached from a wrong side. I shall therefore lay before the Society theory as well as experiment; for the theory is necessary to render the experiment intelligible, although this latter, in so far as it is true, has an independent value, and may be explained by others in some totally different manner.

The difference which chemists draw between the chemical elements and all other bodies, is far greater and indeed of altogether another kind to that which exists between any two compound substances. Other bodies are composed and decomposed; but applied to the elements, these words are altogether inappropriate; when the element is formed there is no chemical synthesis, and when it passes from the free to the combined state, there is no chemical decomposition. This difference the atomic theory expresses by assigning to the two classes of bodies a different molecular constitution. The element it considers as consisting of single and isolated atoms, and all other bodies as systems more or less complex of combined particles. This fundamental difference of conception is well given in the following passage from BERZELIUS*:—"Les atomes d'un même corps élémentaire ne possèdent aucune force de combinaison mutuelle; ils n'adhèrent ensemble qu'en vertu de la force d'agrégation. Plus deux corps élémentaires se ressemblent quant à leurs propriétés chimiques, moins ils tendent à s'unir, et le nouveau corps qui resulte de leur combinaison, a tant d'analogies avec ses éléments constituants, qu'il diffère peu d'un mélange mécanique. Plus, au contraire, les corps élémentaires diffèrent de propriétés chimiques, plus la

* BERZELIUS, Traité de Chimie, Paris, 1845, vol. i. p. 25.

force de combinaison qu'ils exercent les uns sur les autres est grande et plus aussi les propriétés de leurs composés diffèrent de celles de leurs éléments. C'est là un problème dont je ne pourrais entreprendre la solution qu'en traitant de l'influence de l'électricité sur la matière."

This view, although the received doctrine, has not passed quite unquestioned. AMPÈRE invented a molecular theory, which led him to conclusions inconsistent with it. For reasons not of a chemical nature only, but which had reference principally to the propagation of light and sound and to other physical phenomena, he had arrived at the idea that in every chemical substance there were what may be called three forms of matter, the indivisible atom, the molecule or system of atoms, and the particle or system of molecules. He conceived, moreover, that every gas contained in the same space an equal number of these molecules. From this it was a necessary inference, that in that contraction which takes place when oxygen and hydrogen combine to form water, a division must take place of the elemental molecule. He considered that the oxygen divided, half a molecule of oxygen combining with each molecule of hydrogen*. On this view therefore the atoms, even of the elements, formed what was in a certain sense a compound group. The discovery of isomeric forms of hydrocarbon in different states of condensation, and of other similar facts, gave rise to new ideas as to the possible differences of bodies, and explanations similar to that by which the differences between certain isomeric organic bodies have been accounted for came to be applied to the case of the elemental bodies themselves, Thus the allotropy of sulphur has been explained by assuming it, in its various forms, to be the same substance in different states of condensation, in which case the difference between these forms might be expressed by giving to them the different chemical formulæ of S, S_2, S_3. Those physical relations however of density and specific heat, which might give a true scientific value to such speculations, and prove that these substances were really thus connected, have not yet been made out to exist; nor indeed has any fact been discovered which places such a notion beyond a conjecture. GRAHAM again, to explain the mode in which the metals conduct electricity in the voltaic circuit, assigns to these bodies what he terms a sali-molecular structure, and regards them as consisting of two atoms of a chlorous or acid combined with one atom of a zincous or basile element, "the three atoms of the molecule being of one metal and of the same nature†." The latest work in this direction is a paper of M. LAURENT, in which he has attempted, among other things, to account for the differences in the different classes of salts of the same metal in which, hitherto, different oxides of a different degree of saturation have been supposed to exist, by assuming them to contain different molecules or atomic groups of the metal; and he has shown how, on this idea, our classification of chemical substances may be much simplified; on this

* Annales de Chimie, vol. lviii. p. 434. See also GERHARDT, Comptes Rendus des Travaux de Chimie, 1847, p. 90, note.

† See GRAHAM's Chemistry, Ed. 1842, pp. 226 and 541.

view it is necessary to suppose that the present elemental atoms are susceptible of a yet further division*.

These ideas, however philosophical and suggestive, are yet, it must be allowed, very hypothetical. The proof of the compound nature of a chemical substance is of a very simple kind. It lies in the fact, that it has been made by the composition of certain parts, or broken up into those parts, or at least in some phenomena which are supposed to be the evidence of this. Indeed the rational formula of a chemical substance is but a memorandum of its reactions, and a particular mode of expressing the law of the synthesis and analysis of the body, apart from which it has but little meaning. The true nature therefore and chemical formula of the elemental bodies, as of all other substances, is to be discovered by the study of the series of chemical changes in which they are formed, and by the phenomena which they present when they pass into the combined condition. There are even well-known facts of great importance in this point of view, some unexplained, and some, I conceive, misinterpreted.

The point which I shall seek to establish is this,—that at the moment of chemical change a chemical difference exists between the particles of which certain elemental bodies consist, perfectly the same in kind to that which exists between the particles of compound substances under similar circumstances, and on which the phenomena of combination and decomposition depend. That a peculiar chemical relation exists between two particles which combine, is generally admitted and expressed by the term affinity. The electro-chemical theory has defined more exactly in what this affinity consists, and states that the two particles are to one another in a positive and negative electric relation. But I do not know that it has ever been pointed out that this chemical relation—this affinity between the particles of a substance—is an essential condition of the decomposition as well as of the composition of the body. As I am about to infer a chemical difference between the particles of the element from the fact of their chemical separation, I must say a few words upon this point, and I shall simplify the whole question by stating briefly the mode in which I consider chemical change to be effected. I may do this sufficiently for my present purpose in the following propositions:—

1. That when two particles chemically combine, a certain chemical relation exists between them which is expressed by the terms positive and negative. The chemical difference of the particles I term the difference between their conditions in this respect.

2. That when chemical combination takes place between the particles of which any two or more substances consist, a chemical difference exists between the particles of each substance, so that the particles of the same substance are to one another in a positive and negative relation.

3. That the chemical relation between any two particles of these substances is

* Comptes Rendus des Travaux de Chimie, August 1849.

determined by the chemical relation of all the other particles with which they are for the time being associated. Substances, the particles of which are to one another in this peculiar chemical relation, I term chemically polar.

The electro-chemical theory was developed before even the true laws of the propagation of electricity had been discovered, and in the above propositions I have but transferred to chemical change some of the more exact ideas as to the nature of electric action which have since arisen; and we may transfer the ideas and mode of thought without making any hypothesis as to the mutual relation of the phenomena. This is not the place to enter fully on this question, and I shall confine myself to the application of these principles to explain certain phenomena of change in compound substances, to which I shall presently show the parallel in the case of the element. These phenomena are those which go under the name of the "phenomena of the nascent state."

Silver cannot be oxidized by the direct action of oxygen on the metal, but oxide of silver is readily formed by boiling the chloride of this metal with potash. The particles of oxygen and silver have therefore acquired by this association with the chlorine and potassium a chemical relation or affinity which at other times they have not. This is the fact. The rational conception of the fact is given in the expression

$$\underbrace{\overset{+}{\mathrm{Ag}}\,\overset{-}{\mathrm{Cl}}\,\overset{+}{\mathrm{K}}\overset{-}{\mathrm{O}}}=\mathrm{AgO}+\mathrm{K\,Cl},$$

in which I have indicated the polar relation of the substances. The chemical relation therefore between the oxygen and silver is essentially dependent on the chemical relation between the oxygen and potassium, in the same way as a negative and positive electricity are related to each other. The same is true of the relation between any other two particles of the system. Hence chemical decomposition is an essential condition of chemical combination; so that when we see one of these events we may infer the other.

On the other hand, where this polar division of the substance cannot take place, there is no chemical action, or at any rate it takes place with greater difficulty; thus anhydrous sulphuric acid may (as has been shown by MILLON) be distilled off carbonate of potash without alteration, and generally the so-called anhydrous acids have none of the combining properties of the hydrates to which they correspond. The reason of this being, that when these bodies combine they do not decompose, and that it is by the very fact alone of the decomposition of the substance that the combining power is developed in the particles of which they consist, so that in the chemical change which is thus represented—

$$\underbrace{\overset{+}{\mathrm{H}}\overset{-}{\mathrm{SO_4}}\,\overset{+}{\mathrm{K}}\overset{-}{\mathrm{O}}}=\mathrm{HO}+\mathrm{SO_4K},$$

the two combinations which take place are not two combinations accidentally simul-

taneous, but correlative and mutually dependent phenomena which we cannot separate.

In the case of double decomposition, each of the four substances which enter into the change is combined, but it does not appear that this state of combination is necessary to the action. It can take place also, and in the same manner, when the combining substances are only in contact with each other, and not in combination, provided always that there is the right chemical difference between them, which however is essential. Thus, for example, when iodine and phosphorus decompose water (in the usual mode of the formation of hydriodic acid), the chemical relation between the iodine and phosphorus is an essential condition of the action. The same remark applies to the decomposition of water between nitric oxide and chlorine, which can be effected by neither body separately; so that the changes which take place in these experiments are not simply due to the fact that the chlorine or iodine stand in one relation to water, or to the elements of water, and the nitric oxide or phosphorus in another, and that thus the water breaks up, being acted upon by two opposite forces; but that there is also, and must be, a certain chemical difference between the chlorine and nitric oxide and between the iodine and phosphorus, which is as essential and important a condition to the propagation of the action as their relation to the water itself, and indeed without which they could not have this relation. I am not aware that this remark has before been made, nor do I think it likely that it should have been made, but upon the view which I have given, of which it is a consequence.

Facts corresponding to these cases of composition are to be observed, as might be expected, in the decomposition of bodies, for if decomposition be the condition of combination, so of course must combination be the condition of decomposition. FARADAY long since showed that dry carbonate of lime withstands the highest temperatures and is not to be decomposed by heat, but that when a little steam is thrown upon the heated carbonate, decomposition takes place with facility. Why is this? but that the water is the medium for the transference of the polar action which can now take place with the division of the masses: thus—

$$\underbrace{\overset{+}{Ca}\,\overset{-}{CO_3}\,\overset{+}{H}\overset{-}{O}}=CaO+CO_3\,H.$$

I might mention many other examples of the same class.

On the view which I have here given of the nature of chemical change, the very existence of the elemental bodies was a strange and unaccountable anomaly. I have regarded the molecular structure of bodies but as an expression of the law of their synthesis and analysis, and this law again as a result of the peculiar nature of chemical force. It was therefore truly difficult to conceive how an element in the sense of BERZELIUS was formed. The formation of this "uncombined particle" was a fact quite different to the formation of a compound substance, and yet it seemed as unreasonable to suppose that the laws of chemical action should vary in different

materials, as that the laws of motion should be different in different bodies. I therefore considered attentively what we really knew of the laws of chemical change in these bodies. Examples occurred to me, both of the chemical division and chemical synthesis of the elements, by which various phenomena hitherto obscure might be explained. The experiments of the first class prove that a division of the elemental bodies which is known to occur in certain cases of chemical change, is truly a chemical and not simply a mechanical division of these substances. This is shown by the fact that the particles of the element thus separated show the peculiar combining properties of "nascent bodies." It is not necessary to my argument that the precise view which I have given of the nature of this "nascent state" should be admitted; provided only it be allowed, that these properties depend upon the fact that the particle is issuing from a state of combination, which is generally allowed.

1. No theory of chemical change has given rise to more discussion among chemists, than the usual mode of the formation of sulphuric acid by the mutual action of sulphurous acid, nitric oxide, air and water. On this question there are some six recognized theories. The problem is simply this: Why, when the oxygen is made a part of this system of particles, does it possess oxidizing properties which otherwise it has not? On the view I have stated the cause is plain. When nitric oxide acts chemically upon oxygen, the gas is thrown into a polar condition; the result of which is to give to other particles of the mass a combining power, in a direction the reverse of that in which the oxygen combines with the nitric oxide; the change being in all respects analogous to the decomposition of water by the joint action of nitric oxide and chlorine*; thus—

$$\underbrace{\overset{+}{NO_2}\ \overset{-}{O}\overset{+}{O}\ \overset{-}{SO_2}}=NO_3+SO_3.$$

The best of the other explanations of this fact is, in my opinion, that of PÉLIGOT†, who considers the formation of the sulphuric acid to be the result of the successive formation and decomposition of nitric acid. This, however, does but shift the difficulty to another point; for why does nitric acid oxidize sulphurous acid? In truth, in this case, a perfectly similar polarization takes place within the acid itself—

$$(NO_5=)\underbrace{\overset{+}{NO_3}\ \overset{-}{O}\ \overset{+}{O}\ \overset{-}{SO_2}}=NO_4+SO_3.$$

* In the following experiments I am compelled to call by the same name three very different things—the isolated element, the particles of the element at the moment of their chemical separation or synthesis, and the combined element; and I wish to observe, that when I state that there is a chemical difference between the particles of the element, I mean simply the particles of which the element consists. The chemical nature of these particles is a further question.

† Annales de Chimie, 3rd Series, vol. xii. p. 266. PÉLIGOT states that nitric oxide always forms hyponitric acid and no nitrous acid, in contact with atmospheric air; but it by no means follows, even if this be the substance formed with atmospheric air alone, that the same substance is formed in the presence of sulphurous acid; indeed, on the view I have given, a difference in the reaction would rather be anticipated.

For the formation of the hyponitric acid from the nitric acid is just as much the formation of a new chemical substance as if it were made by the direct action of oxygen upon nitric oxide, and is attended with a similar division of the oxygen. But this stage of the formation of nitric acid is useless, and not necessary to the conception of the change; for there are other perfectly parallel cases which do not admit of such an explanation.

2. I will take the formation of chloro-sulphuric acid, in the remarkable experiment by which REGNAULT prepared this body*. Olefiant gas, as usually prepared from alcohol and sulphuric acid, contains a large quantity of sulphurous acid; when chlorine is brought in contact with this mixture of gases, two substances are formed, chloro-sulphuric acid, SO_2Cl, and the Dutchman's liquid, $C_4H_4Cl_2$. Upon sulphurous acid alone (in the circumstances under which the experiment is made) chlorine has no action whatever, nor, according to REGNAULT, upon olefiant gas, when both gases are dry, and only in diffused daylight. The formation, therefore, of this body is due to the polar division of the chlorine, just as the formation of sulphuric acid to the polar division of the oxygen; the olefiant gas being to the chlorine in the same relation as the nitric oxide to the oxygen in the other experiments, so that we may conceive the change to take place thus—

$$\underbrace{\overset{+}{C_2}H_2\overset{-}{Cl}\overset{+}{Cl}\overset{-}{SO_2}}=C_2H_2Cl+Cl\,SO_2.$$

This example is not open to those objections which, from the formation of the oxides of nitrogen, might be raised to the other instance, for here the combinations mutually determine each other. With water, the chloro-sulphuric acid decomposes with the formation of sulphuric and hydrochloric acids; but through this experiment we can distinctly trace back the cause of the formation of the sulphuric acid, in this, as in the more usual mode of its formation, to the polarization of the element; and on considering attentively the mode of the formation of chemical substances, it may be seen that the formation of a large class of compounds, among which are the oxides of chlorine and iodine, is ever preceded by a similar fact.

3. It is well known that when a mixture of hydrogen and any oxide of nitrogen† is passed over heated spongy platinum, the oxide of nitrogen is decomposed and ammonia and water formed. Were the hydrogen a compound substance, it would be thought that the simultaneous formation of these substances was sufficiently explained, by saying that it was a case of double decomposition, and it is indeed the same phenomenon; thus—

$$\underbrace{\overset{+}{N}\overset{-}{O_3}\overset{+}{H_3}\overset{-}{H_3}}=3HO+NH_3,$$

the hydrogen being "*nascent*" from itself.

* Annales de Chimie, 2nd Series, lxix. p. 170, and lxxi. p. 445.

† See KUHLMANN, LIEBIG's Annalen, vol. xxix. p. 286.

4. We know from the researches of H. Rose, that in a neutral solution of the bichloride of mercury, the mercury is precipitated on zinc in the form of a black powder, but on the addition of an acid the metal becomes bright and the zinc is amalgamated*. The addition of bichloride of mercury also instantly stops the most violent evolution of hydrogen from the action of hydrochloric acid upon zinc, with the formation of the same amalgam. These curious experiments, which certainly caused much surprise in Rose, become intelligible from the considerations which I have mentioned. The combination of zinc with mercury is a combination in a different direction to that of the zinc with chlorine, hence the latter determines and causes the first; thus—

$$\underbrace{\overset{+}{\mathrm{H}}\,\overset{-}{\mathrm{Cl}}\,\overset{+}{\mathrm{Zn}}\,\overset{-}{\mathrm{Zn}}\,\overset{+}{\mathrm{Hg}}\,\overset{-}{\mathrm{Cl}}}=\mathrm{H\,Cl}+\mathrm{Zn\,Hg}+\mathrm{Zn\,Cl}.$$

5. A very beautiful illustration of the way in which one chemical combination determines another, is seen in another experiment with the same metal. Zinc, it is known, decomposes slowly, with evolution of hydrogen, a strong and boiling solution of caustic potash; but when into the solution a few crystals of nitre or nitrite of potash are thrown, the zinc is rapidly dissolved with the evolution of ammonia. The reason of this I consider to be, that the polar division of the zinc now takes place with the greatest facility, the zinc being oxidized in two directions; the zinc decomposes the water, by which a polarity is given to the hydrogen, which causes it to combine with the nitrogen of the nitric acid to form ammonia, by which combination the other particles of the nitric acid become in their turn polar and oxidize again the zinc; the action, as it were, proceeding from and returning back again to that element. The change, for example, may be represented thus:—

$$\underbrace{\overset{+}{\mathrm{H}_3}\,\overset{-}{\mathrm{O}_3}\,\overset{+}{\mathrm{Zn}_3}\,\overset{-}{\mathrm{Zn}_3}\,\overset{+}{\mathrm{O}_3}\,\overset{-}{\mathrm{N}}}=\mathrm{NH}_3+6\mathrm{ZnO}.$$

6. To the preceding experiments I will only add the phenomena of substitution, which, viewed in relation to them, assume a new form. The division of the chlorine which takes place in substitution is a very similar fact to that distribution of the element which takes place in the formation of chloro-sulphuric acid (which I have before cited), and admits of a similar explanation. The problem is, why, with even the smallest quantity of chlorine, does a portion of the chlorine ever combine with the organic body? Why is the hydrogen never simply removed? The solution is, that one of these two changes determines the other, precisely as the combination with olefiant gas determines the combination with sulphurous acid. Nor do I see what intelligible distinction is to be drawn between the action of chlorine on the organic body and that of hydrogen on nitric oxide, or between either of these two cases and that of water itself on chloro-sulphuric acid. The organic body behaves as though it were a simple compound of hydrogen on the one hand, and the remaining ele-

* Liebig's Annalen, vol. lxiv. 283.

ments of the system on the other, and this, during the action and under the influence of the chlorine, it may truly be.

If it be true that in the preceding experiments this polar division of the element takes place, (a division, at any rate, in many points analogous to the decomposition of the compound body when no elemental substance is isolated, but the particles are transferred from one system to another,) it cannot but be, that in the *formation* of the element the correlative fact is to be observed, and that the element itself is made by the synthesis of polar particles. This is indicated by theory, and although the more usual mode of forming these elemental bodies is not such as to bring to light the true nature of this synthesis, there are other, although as yet rarer, instances of the formation of these bodies, which not only are not opposed to this view, but prove it.

1. When an acid is added to a perfectly pure solution of an alkaline iodide, such as may readily be procured by precipitating any iodate it contains by baryta water and filtering, the solution remains perfectly clear. Neither, when an acid is added to a pure solution of iodate of potash, is there any alteration, but on mixing these solutions an abundant precipitate of iodine is formed. It is said that the iodate and iodide of zinc, without acid, undergo a similar decomposition. It is very plain that these changes are simple cases of what is called double decomposition. The hydriodic and iodic acids decompose one another, and it is my opinion that in the change

$$IO_6H+5HI=6HO+6I,$$

whatever be that combining relation which subsists between the oxygen and hydrogen, that same relation must also be between the particles of the iodine itself. What is commonly called the affinity of hydrogen for oxygen is not sufficient to account for this change, for hydrogen alone will not decompose the iodic acid, unless it be in the nascent condition. When hydrochloric acid is the decomposing body, chloride of iodine is formed, when hydriodic acid, the iodine itself. Are we not to admit that these two substances are formed according to the same law? To this synthesis of the iodine, the division of the element which takes place at the formation of the hydriodic and iodic acids, is the correlative fact, to explain which we must assume the same polar difference between its particles (see page 765).

2. In the course of his researches on the hypophosphites, WURZ discovered a very singular substance, the hydruret of copper*. This substance is formed by the action of hypophosphorous acid upon copper salts. It readily decomposes, so that it is not easy to determine its constitution, but his analyses very closely corresponded with the formula Cu_2H. That this is truly the formula of the substance, may be inferred with yet more certainty than from the analyses, from the following curious reaction.

* BERZELIUS attempted to throw some doubt upon the existence of this body, but the correctness of the facts, as stated by WURZ, is guaranteed, not only by the well-known skill and ability of this chemist, but also by the fact that POGGENDORFF had succeeded in procuring a hydruret of copper by the electrolysis of the sulphate of this metal.

In contact with strong hydrochloric acid hydrogen is evolved, and the protochloride of copper, $Cu_2\,Cl$, formed. Both substances are decomposed, and WURZ satisfied himself, and gives the experiments, which show that the volume of the hydrogen evolved was the double of that due to the simple decomposition of the substance. I will add the remark which he makes on this experiment:—"On sait que l'acide chlorhydrique n'attaque le cuivre qu'avec une extrême difficulté, et la presence de l'hydrogène, loin de favoriser la réaction, devrait, d'après les lois de l'affinité, y ajouter un nouvel obstacle. La décomposition de l'hydrure de cuivre par l'acide chlorhydrique paraît donc s'effectuer en vertu d'une action de contact*."

This fact, the conception of which offers these theoretical difficulties, becomes perfectly intelligible, and indeed might have been predicted from the principles I have laid down. The decomposition is perfectly similar to that of the suboxide of copper under analogous circumstances, arises from the same cause, and may be expressed thus—

$$\underbrace{\overset{+}{Cu_2}\,\overset{-}{H}\,\overset{+}{H}\overset{-}{Cl}}=Cu_2\,Cl+H_2.$$

This experiment enables us to see clearly the cause of a class of decompositions very analogous to it, and which have presented similar theoretical difficulties†. An alloy of platinum and silver will dissolve in nitric acid, which will not act upon the platinum alone; acids will, in like manner, dissolve the alloy of copper and zinc‡, which on the copper alone have no action. Now the hydruret of copper is itself, in its chemical relations, an alloy, and the action of the acid on the alloy of copper and zinc is a fact very analogous to the action of the hydrochloric acid upon this body, and the explanation of this fact involves similar phenomena; thus—

$$\underbrace{\overset{+}{H}\,\overset{-}{Cl}\,\overset{+}{Zn}\,\overset{-}{Cu}\,\overset{+}{Cl}\,\overset{-}{H}}=Cl\,Zn+Cu\,Cl+H_2,$$

the polar composition of the hydrogen being essential to the comprehension of the experiment. A further confirmation of this view is found in the decomposition by water of the remarkable bodies discovered by FRANKLAND§, to which he has given the names of zinc-methyl and zinc-ethyl. The theoretical analogy of these bodies to the hydrogen compounds of the metal is perfect, and with water they give a precisely similar reaction to that of the hydruret of copper with hydrochloric acid. Zinc-ethyl, for example, breaks up thus—

$$\underbrace{\overset{+}{Zn}\,\overset{-}{C_4\,H_5}\overset{+}{H}\overset{-}{O}}=C_4\,H_5\,H+ZnO,$$

in which decomposition the hydrogen and the hydrocarbon (which is the analogue of

* Annales de Chimie, 3rd Series, vol. xi. 251.

† These facts have been cited by LIEBIG with another view. LIEBIG's Annalen, vol. xxx. p. 262.

‡ GMELIN's Handbuch, vol. iii. p. 448.

§ Journal of the Chemical Society, January 1850.

hydrogen) are to one another in the same polar relation, and fulfill the same part in the change as the two equivalents of the hydrogen itself in the decomposition of the hydruret.

3. When a solution of bichromate of potash is poured into a strong and acid solution of the peroxide of barium in hydrochloric or nitric acid, a violent effervescence and escape of oxygen takes place; apart, these solutions are perfectly stable; bring them together, they are both decomposed; the chromic acid passes into chloride of chrome, the peroxide of hydrogen into water, and the oxygen formed is due to the simultaneous decomposition of both bodies, thus—

$$3ClH+2Cr\,O_3+3HO_2=Cr_2\,Cl_3+6HO+3O_2.$$

I certainly regard the oxygen itself, in this experiment, as the true reducing agent, and I believe that the chromic acid is decomposed by the oxygen of the peroxide of hydrogen, according to the same law of decomposition, and for the very same reason, as it would be by hydrogen itself if a piece of zinc were thrown into the acid solution, this reason being the polarity of the particle induced by chemical change. In this experiment is brought before us, in a very forcible manner, the very slight difference which truly separates the phenomena of oxidation and reduction, which are usually regarded as so distinct. In speaking of the formation of sulphuric acid, I have said that the oxidation of sulphurous acid by nitric acid is to be attributed to a polar condition of the oxygen liberated from the nitric acid, which polar condition is induced by the formation of hyponitric acid within the system of which it forms a part. Now the formation of water in the peroxide of hydrogen is a fact precisely similar to the formation of the hyponitric acid in the nitric acid, and it might reasonably be anticipated that this oxygen would have a similar oxidizing power. This is in truth the case; for when the temperature is low, the solutions dilute, and the experiment carefully managed, no gas is given off, but a deep blue solution is formed, containing perhaps, as stated by BARRESWIL*, who first examined this reaction, a higher oxide of chrome. This solution however rapidly decomposes, oxygen is evolved, the blue colour disappears, and the final result is the same as if the compound had never been formed. When manganate of potash, peroxide of manganese and various other substances are substituted for the chromate of potash in this experiment, a similar decomposition takes place, but without any signs of the intermediate stage of oxidation. Under other circumstances the oxidation and reduction may be separated. Thus, when peroxide of barium is thrown into an acid solution of the prussiate of potash, the prussiate is oxidized and the red prussiate is formed. When, on the other hand, the same experiment is made with the alkaline or neutral solution of the red prussiate, oxygen gas is given off in abundance from the peroxide of barium as well as from the red prussiate, and the latter passes into prussiate. On adding to this solution an acid solution of perchloride of iron, care being taken that

* Annales de Chimie, vol. xx. p. 364.

the whole of the peroxide of barium is decomposed, prussian blue is produced in abundance. In this experiment one atom of oxygen is first added, and this atom is then removed by the contact of another atom under suitable circumstances. I infer therefore from these experiments, not that the oxidation is a necessary antecedent to the disoxidation, but that the spontaneous decomposition of the oxidized body and the reduction of the chromic acid, where no oxidation takes place, and the oxidation of the body, are due to one and the same cause, namely, to the mutual attraction of the elemental particles. When, for example, arsenious acid is oxidized by the action of chlorine, I consider that the oxygen is oxidized as well as the arsenic. We are led to the same conclusions by various well-known experiments; in the case, for example, of the decomposition of the nitrate of ammonia on boiling, when this compound breaks up into water and nitrogen, thus—

$$\underbrace{\overset{+}{N}\overset{-}{O}_4\overset{+}{H}_4\overset{-}{N}}=4HO+N_2;$$

while from no point of view is it very logical to draw a distinction between two facts so very similar as the formation of the water and the nitrogen, it is proved, by the experiments I have cited, that the mutual attraction of the particles of the nitrogen is a most important condition of the change.

The transition from these cases of spontaneous decomposition to other instances, in which no one of the substances usually called compound is formed, but the elements alone are liberated, is obvious; and I cannot but think that these phenomena, viewed as the last of a series of chemical changes, proceeding from the simplest case of double decomposition to the curious experiments I have just cited, each successive link of which is bound to the preceding by the closest analogies, reasonably admit of a very different interpretation to that which we should put upon them when regarded out of this connection. It is hard to draw a distinction between the decomposition of the chloride of nitrogen and of the nitrite of ammonia. From quite independent considerations, the conclusion is forced upon us, that the mutual attraction of the particles of chlorine and of nitrogen plays a most important part in other cases of chemical change. Why may we not admit that in this case the decomposition is determined solely by these relations? The heat which attends upon this and other similar decompositions is, on the electro-chemical theory, as confessed by its greatest supporters, an inexplicable enigma. Heat is the constant sign of combination, but here it asserts is only decomposition, so that theory and fact are plainly at issue. On the other hand, admitting that in this experiment the formation of the elements is a true chemical synthesis, the evolution of heat is accounted for; and as the elements, chlorine and nitrogen, are far more permanent forms of matter, and less readily altered by chemical action than the chloride of nitrogen, so it is reasonable to believe that the particles of which they are composed are in a far more intimate state of combination. The transition from these experiments to the most ordinary cases of the formation of

the element is obvious, it being plain that the reduction of oxide of silver* into oxygen gas and the metal, differs only from the spontaneous decomposition of the chloride of nitrogen in the temperature at which it takes place.

In the preceding statement, I have used the word polar to express that alternate difference of the condition of the particles by which I conceive chemical action to be propagated. It is no objection to the use of this word that it is undefined, and that I have not pointed out in what this difference consists. It may be a real difference, which we can use for purposes of thought and inquiry, and yet an unknown difference, to which we cannot at present assign a true value. A more serious objection lies in the way in which this word has been misused, and the false associations which, in some minds, are connected with it. It is, however, not difficult for those who must ultimately fix the meaning of this term, to draw the distinctions necessary to its right application; and as I myself have found the word very useful, and also found that through the associations which are rightly connected with it, it conveyed to some persons, whose opinion was well worth considering, an idea which could not otherwise have been so simply given, I have here used it. At the same time let me observe, that that to which I wish to direct the attention of chemists, is to a new analogy between certain chemical changes and to the correlation of phenomena which have not before been grouped together, and, provided that analogy and relation be recognized, the word by which it is expressed is of less importance†. I now proceed to an experimental inquiry which originated in the considerations I have here given.

The discoverer of the peroxide of hydrogen, THÉNARD, observed certain singular and remarkable properties of this compound, of a kind altogether new and calculated to fix the interest and attention of chemists. To prepare the peroxide of hydrogen, according to his directions, is a process so troublesome and tedious, that it may have deterred chemists from the further and full investigation of these phenomena. It is at any rate to THÉNARD alone that we owe whatever knowledge we possess of this singular body. Since his investigation, which dates from the year

* In certain cases we can trace the very mode in which this decomposition by heat takes place. Thus in the decomposition of chlorate of potash by heat, the true way in which this substance is decomposed is, as discovered by SERULLAS, the decomposition of one particle by the next. The chlorate is first oxidized to perchlorate, and this perchlorate, as shown by MILLON, again reduced to chlorate with evolution of oxygen. Thus the action proceeds by a continual oxidation and reduction of the substance, the phenomena being very similar to the oxidation of the chromic acid by the peroxide of hydrogen and the spontaneous decomposition of the compound formed. By mixing the chlorate of potash with oxide of copper, the formation of the perchlorate is entirely prevented, and the action converted into one of spontaneous decomposition.

† The idea of polarity has been applied to the explanation of chemical phenomena by other chemists as well as myself. I may refer especially to LÖWIG's Introduction to his Organic Chemistry (vol. i. p. 1. Edition 1845). GRAHAM also has given, in the last edition of his Treatise on Chemistry, a chapter on Chemical Polarity. It would be out of place to enter here on any criticism of their views or comparison of them with my own, but I give the reference for those who may be desirous to see the way in which others have treated this subject.

1818, no new fact of the slightest importance has been added to its history. The properties however of which I speak, can all be observed with the solution of the peroxide of barium, in hydrochloric or acetic acid, which can be readily prepared. The properties of this solution are different according as it is alkaline or acid. The alkaline solution is of an unstable nature; even at ordinary temperatures it continually loses oxygen, and on heating undergoes rapid decomposition. The acid solution is more permanent, may be long kept without sensible alteration, and may even be heated to the boiling-point with no evident evolution of gas. Either solution, however, is violently decomposed when certain substances (among which finely divided carbon or platinum are very effective) are thrown into it. In these cases the peroxide is decomposed, while the carbon and platinum remain, as far as we know, unaltered. There are however other bodies which cause this decomposition with perhaps greater energy, and themselves undergo a chemical change of the most surprising nature; these bodies are all those metallic oxides which can readily be reduced,—the oxides of gold, and silver and mercury, and the peroxides of lead, manganese, nickel and other similar substances. These bodies decompose the solution, as does platinum or carbon, while the substances themselves also, during the decomposition, lose oxygen, and are reduced either to a metal or to a lower degree of oxidation. The solution, whether acid or alkaline, is ever decomposed by these bodies; but the facility with which the substance itself is reduced, and in some cases whether this reduction takes place at all, depends upon the neutral or acid condition of the solution, and varies with the particular substance taken in a way on which it is not now necessary to dwell. The decomposition caused by platinum and carbon, however strange, is not quite without parallel. But the simultaneous reduction of the peroxide of hydrogen and the oxide of silver is a solitary fact, by the side of which chemists have been able to place scarcely an analogous much less a similar instance. Yet eminent chemists have offered an explanation of these phenomena, and if these are adequate, further inquiry is unnecessary. I shall not criticise the absolute or the relative value of these explanations; but they add so much to the interest of the question, so clearly show the difficulties under which chemical theory has laboured in dealing with these facts, and also, as I believe, how inadequate it has proved to meet them, that I shall briefly mention the most remarkable.

The following quotation gives the impression made by these facts upon THÉNARD, who first discovered them:—

"Quelle est la cause des phénomènes que nous venons d'exposer? Voilà maintenant ce qu'il s'agit de rechercher. Pour cela qu'il nous soit permis de rappeler ceux que présentent l'oxide d'argent et l'argent avec le nitrate oxigéné neutre du potasse. L'argent très divisé dégage rapidement l'oxigène de ce sel; il ne s'altère point, et le nitrate oxigéné devient nitrate neutre.

"L'oxide d'argent dégage plus rapidement encore que l'argent l'oxigène du nitrate oxigéné; lui-même est décomposé, il se réduit, l'argent se précipite tout entier, et l'on

ne retrouve dans la liqueur que du nitrate neutre de potasse ordinaire. Or, dans ces décompositions, *l'action chimique est évidemment nulle*; il faut donc les attribuer à une cause physique; mais elles ne dépendent ni de la chaleur, ni de la lumière; d'ou il suit qu'elles sont probablement dues à l'électricité. Je chercherai à m'en assurer d'une manière positive; je chercherai aussi à savoir si la cause, quelle qu'elle soit, ne pourrait point être produite par le contact de deux liquides, et même de deux gaz. De là, découlera peut-être l'explication d'un grand nombre de phénomènes*."

An idea as to the possible cause of these phenomena was thrown out, some years back, by another distinguished French chemist, DUMAS, which, although but an incidental observation and unaccompanied with any experimental research, has a special interest as giving the scientific conception of these facts from the electro-chemical point of view, from which this chemist then regarded them.

"La répulsion que les molécules de même signe exercent l'une sur l'autre, répulsion qui nous a servi à expliquer plus haut les effets qu'on observe dans la formation des composés multiples, va nous servir maintenant à expliquer aussi ceux que l'on observe entre deux corps qui contiennent un excès de molécules semblables. Ces corps tendent à se décomposer mutuellement par suite de cette action répulsive.

"En effet c'est ainsi qu'on peut se rendre compte de l'action des acides sur beaucoup de peroxides qui perdent sur leur influence une partie de leur oxygène, c'est ainsi qu'on peut concevoir l'action si bigarre et si remarquable de l'eau oxygenée sur certains oxides. Ce composé perd par le contact de l'oxide d'argent, par exemple, la moitié de son oxigène repasse à l'état d'eau, *chasse* l'oxigène de l'oxide et le ramène à l'état métallique. Quant on envisage ce simple fait avec les anciennes idées de l'affinité, il est inintelligible, tandis qu'avec les idées électriques il pouvait en quelque sorte être prévu†."

Another view has been put forward by LIEBIG. These experiments with the peroxide of hydrogen he places by the side of the fermentation and decay of organic bodies, of which chemical changes he thus gives the cause‡:—"The cause," says he, "is the power which a body possesses in the act of decomposition or composition to elicit the same action in a body in contact with it, or to render it capable of undergoing the same change which itself experiences. Thus the decomposition of the ferment decomposes also the sugar, and the decomposition of the peroxide of hydrogen decomposes the metallic oxide." The simultaneous decomposition of the two substances is the fact. That it is the very chemical change itself in the one instance which determines the chemical change in the other; this relation LIEBIG has pointed out. But why and how, consistently with what we otherwise know of the nature of chemical action, and the mode of its transference and propagation, this can be the

* Annales de Chimie, 2nd Series, vol. ix. p. 98?

† DUMAS, Chimie Appliquée aux Arts, vol. i. Introduction, p. 64.

‡ LIEBIG's Annalen. vol. xxx. pp. 280, 262 and 279.

case, is a problem which remained to us, and which, in the case of one at least of these experiments, it was my hope to solve.

Hitherto, in the breaking up of the oxide of silver and the peroxide of hydrogen, no chemical fact has been recognised but the simultaneous decomposition of two chemical substances. This is that fact for which it has been so difficult to account. Were it, for example, a hydride of silver which was thus decomposed and water formed and not simply oxygen, the experiment would have attracted no attention. On the view I have given, the formation of the oxygen itself is as truly a chemical synthesis as the formation of water, and may be substituted for it in a chemical change. This supplies an explanation of these facts at once adequate and simple; the oxide of silver in this experiment being reduced by the oxygen of the peroxide of hydrogen, just as in other cases it might be by hydrogen; the formation of the silver from the particles of which it is composed being the corresponding fact in the decomposition of the oxide of silver to the formation of water in the peroxide, so that we may represent the change thus:—

$$\underbrace{\overset{+}{H}\overset{-}{O}\,\overset{+}{O}\,\overset{-}{O}\,\overset{+}{Ag}_{\frac{1}{2}}\,\overset{-}{Ag}_{\frac{1}{2}}}=HO+O_2+Ag.$$

No one can be more sensible than I am of the wide interval which exists between such a mode of representing a chemical change and an ascertained fact. The very form in which I have just expressed the decomposition involves an important assumption, an assumption indeed on which, in my opinion, the whole question rests. If it be true that these bodies are thus decomposed in definite and equivalent proportions, and that the simultaneous decomposition of the bodies proceeds according to this law, it is impossible to deny the chemical relation of these changes and the mutual chemical action of the substances; and, on the other hand, if the formation of this oxygen is to be regarded as a true chemical synthesis, this synthesis must follow the universal law of the formation of chemical substances, and the masses must combine in definite and equivalent proportions. It is only the apparent absence of this relation between the decomposing bodies which removes fermentation from ordinary chemical changes, and causes its chemical nature to be denied; and in that parallel which LIEBIG draws between these decompositions and fermentation, it is tacitly assumed that in this case also, as well as in the case of fermentation, no such relation exists. The following words of LIEBIG, from the paper I have already referred to, clearly show this point:—"A certain quantity of ferment is required to cause fermentation in a portion of sugar; its action however is *no action of mass*, but is entirely limited to its presence up to that moment when the last atom of sugar is decomposed. It is therefore no peculiar body, no substance or matter which effects decomposition, but these are the carriers of an activity* which extends itself over the sphere of the decomposing body."

* "Träger einer Thätigheit." LIEBIG's Annalen, vol. xxx. p. 279.

It was therefore the quantitative relation of the decomposing substances which seemed to me the essential point to be determined, and which experiment alone could decide; for it was quite possible (and indeed had been taken for granted) that the action varied according to some other law. It might have none of the characters of a chemical change; it might, for example, vary directly with the acting masses, or with the temperature alone, or be a function, so to say, of so many variables that the true law of action would be altogether hidden.

Preparation of the Peroxide of Barium.

The baryta used in the following experiments was prepared by the ignition of the pure nitrate in a crucible of fine white earthenware. This was protected externally by a common earthenware crucible, and the space between the two filled up with crucible dust. The nitrate was thrown gradually into the crucible, one portion being thoroughly decomposed before the addition of the next. Baryta, as commonly prepared, contains large quantities of peroxide, as may readily be ascertained by dissolving in hydrochloric acid and adding bichromate of potash to the solution; and a very long and strong ignition is necessary to drive off the last portion of oxygen. The purest baryta is not porous, but perfectly compact, very heavy, and of the crystalline grain of fine marble. The baryta thus prepared contains traces only of matter from the crucible, the adhering particles of which are to be carefully broken off, and hardly any impurities, but a little water, and a very little carbonic acid. If an ordinary Hessian crucible be used for its preparation, as was the case with the baryta used in some of the earlier of my experiments, the baryta will be very impure.

To prepare the peroxide, oxygen was passed over the baryta, broken into pieces of the size of a small pea and placed in a combustion-tube, which was heated in an ordinary charcoal trough. The oxygen was made from peroxide of manganese and carefully freed from carbonic acid, and dried before entering the tube. The gas was contained in a gas-holder so as to regulate the current, and was passed over the peroxide, after all absorption had ceased, until the tube was cool. The temperature necessary for the absorption is a low red heat, which is not to be exceeded, as a portion of oxygen is given off at a higher temperature. The operation may be distinctly followed through the tube, the baryta glowing when the stream of gas comes in contact with it. The absorption is both rapid and complete; and I have repeatedly made the experiment of attaching to the end of the tube, where the oxygen not absorbed would pass out, a small tube dipping into mercury, and have found that the experiment can readily be so regulated that a considerable stream of gas will enter at one end of the tube and not a bubble pass out at the other; and indeed the absorption was often so rapid that the gas was absorbed faster than it entered, and the mercury rose several inches in the tube; the whole oxygen therefore is absorbed.

The peroxide presents after the experiment a mass of uniform texture and appearance, and is very white, the baryta itself being of a darker colour. A little of the

powdered substance, moistened with water on the back of the hand, gives no sensible heat. The peroxide was carefully freed from any adhering glass, or pieces in which the absorption was incomplete, from which it may be distinguished by the colour, and was preserved in stoppered bottles over sulphuric acid; a precaution which was desirable, as the preparations had to be preserved for a long time without any alteration in the per-centage of oxygen.

The peroxide of barium thus obtained is a perfectly stable body. When dry, it is only a very intense heat which can drive off its oxygen. It is nearly insoluble in water, the filtered solution giving no gas with oxide of silver, which would be the case if any substance were dissolved; and when preserved from the action of the carbonic acid of the air, it may be long kept even in water without any sensible evolution of gas. When the powdered substance is even boiled with water, no gas is given off; and after long boiling, on examining the dried residue, I have found that the effect of boiling has actually been to increase the per-centage of oxygen, the baryta, of which a certain quantity is always present, being dissolved. These facts are contrary to the usual statements*, and probably this stability only belongs to a very pure substance, for a small quantity of the oxides of iron or of manganese would alter these reactions.

The peculiar experiments of the reduction of the metallic oxides, as stated by Thénard and other chemists, are referred to the peroxide of hydrogen; and it is on the peculiar instability of this body that the explanation of Liebig of these phenomena rests, the spontaneous decomposition of the peroxide being considered as antecedent to and necessary to set up the action in the other substances. I was however anxious to see whether the peroxides of metals themselves would not produce similar effects; and on placing the peroxide of potassium (the mass which is produced by the action of potassium on melted nitre) in contact with moist chloride of silver in water, I found that the chloride was reduced, just as it might be by zinc, and oxygen evolved; and the same takes place with the iodide, bromide, cyanide, nitrate and oxide of silver and with other metallic combinations. Water alone, as is well known, decomposes the peroxide of potassium; this body therefore was in a similar unstable state to that supposed in the peroxide of hydrogen; but on extending my experiments to the peroxide of barium itself, I found that all the reductions which could be made with the peroxide of hydrogen, took place with this body also with the greatest facility. Finely-divided platinum, silver or carbon, decompose it, but far less rapidly than those substances which are themselves also decomposed. I will not here discuss the general chemical reactions of this peroxide, but defer their consideration until I can treat with advantage, in a more exact manner, of the general theory of this action.

The facts I have just mentioned gave a direction to my experiments, and instead of the peroxide of hydrogen, the preparation and preservation of which involved many difficulties, and with which it was inconvenient to work, I determined to use, in the experiments I proposed, the peroxide of barium itself.

* See Barium superoxyd, Handwörterbuch der Chemie, vol. i. p. 667.

Before the study of these decompositions was possible, it was necessary to have some ready and accurate method of determining the amount of oxygen in the various preparations of the peroxide, which could never be obtained absolutely pure and corresponding to a theoretical formula, and of which I cannot indeed find that any satisfactory analysis has yet been made.

After various experiments I selected two methods, which combined the advantage of great facility of execution with perfect agreement in their results. One of these methods depends on the chemical change which takes place when the peroxide of barium is brought in contact with an acid solution of chromic acid, when, as I have before mentioned, both the peroxide and the chromic acid are decomposed with evolution of gas. Supposing this to be a definite and constant reaction, we have, it is evident, in the evolved gas, a measure of the oxygen in the peroxide, from which, if the reaction were known, the latter might be calculated. For this, however, it was necessary first to discover the nature of the decomposition. The other method depends on the decomposition of the acid solution of the peroxide by finely-divided platinum or carbon, in which case the oxygen evolved is plainly half the total oxygen in the peroxide itself. For the determination of the oxygen in the preparation of a small quantity of the peroxide, it was quite practicable to weigh the baryta before and after the absorption of the gas; and although this plan could not be applied to those larger quantities of the substance which it was desirable to prepare at once, yet, as there could be no doubt as to the general accuracy of the determination if the experiment were conducted with care, I availed myself of it for determining the reaction in question with chromic acid, and for a general control over the methods. The baryta was placed in a platinum tube about 8 inches long and half an inch wide, and the whole experiment conducted precisely in the manner already described in the preparation of the peroxide. The tube was first weighed empty, the ends being closed with dry corks, again with the baryta, and again after the experiment. The peroxide was then rapidly pounded and used for the other determinations. A glass tube cannot be used for this experiment, as the glass is always slightly acted upon, where in contact with the baryta, which, although of little consequence in an experiment on a large scale, as causing an impurity in the peroxide, yet gives rise to a discrepancy between the amount of oxygen calculated from the absorption and the percentage of oxygen deduced from the other experiments.

Two experiments, conducted in this manner, gave the following results:—

A. 12·581 grms. of baryta increased in weight 0·952 grm., corresponding to an increase in weight of 7·53 on 100 parts.

B. 15·180 grms. of baryta increased in weight 1·111 grm., corresponding to an increase in weight of 7·318 on 100 parts.

Hence the two preparations of peroxide of barium contained respectively—

Preparation A, 7·03 per cent.; preparation B, 6·81 per cent. of oxygen in addition to the oxygen of the baryta.

The experiment with the acid solution of chromic acid was made thus:—a weighed quantity of the peroxide was mixed with a very large excess of powdered bichromate of potash in a small flask, such as is often used for the determination of carbonic acid, provided, that is, with a drying tube (in this case filled with small pieces of caustic potash) and a small tube reaching to the bottom of the flask, through which a little air might be drawn after the conclusion of the experiment. Strong hydrochloric acid was contained in the usual small tube, and the whole experiment, in short, conducted precisely as a carbonic acid determination. It is essential to the accuracy of the experiment that care should be taken to have present a great excess of bichromate (at least three or four times the weight of the peroxide taken), an excess of acid, and also to have fresh potash in the drying tube, as there is a considerable rush of gas, and a little carbonic acid or water might otherwise pass through the tube. The peroxide, however, in a good preparation contains a mere trace of carbonate; and I have made the experiment of passing the gas from the potash tube through baryta water, and have found that no carbonic acid escaped the apparatus, with a far more violent evolution of gas than need take place in the experiment.

I. 2·1015 grms. of the preparation A. gave a loss of 0·243 grm., corresponding to a loss of 11·56 on 100 parts of the substance taken.

II. 2·1265 grms. of the preparation A. gave a loss of 0·252 grm., corresponding to a loss of 11·85 on 100 parts of the substance.

III. 2·2127 grms. of the preparation B. gave a loss of 0·268 grm. corresponding to a loss of 12·11 on 100 parts of the substance.

IV. 2·0975 grms. of the preparation B. gave a loss of 0·259 grm., corresponding to a loss of 12·34 on 100 parts of the substance.

V. 2·0395 grms. of the preparation B. gave a loss of 0·243 grm., corresponding to a loss of 11·91 on 100 parts of the substance.

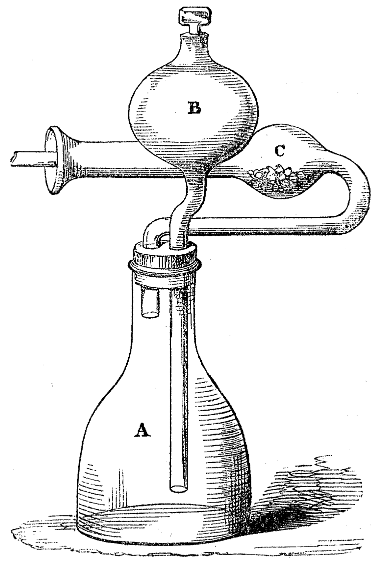
From these experiments it results that in this reaction the chromic acid loses three and the peroxide four equivalents of oxygen, that is, that the total loss is to the loss from the peroxide as 7 : 4. For calculating on this hypothesis the amount of oxygen in the two preparations, we find for the preparation A. from experiments I. and II. respectively, 6·60 and 6·67 per cent. of oxygen, and for the preparation B. from experiments III., IV. and V., 6·91, 7·05 and 6·80 per cent. of oxygen, which are the numbers given in the other experiments. The reaction would therefore be represented thus—

$$2Cr\,O_3+4Ba\,O_2=Cr_2\,O_3+O_7+4BaO.$$

This method has the advantage of giving a considerable loss of oxygen with a small quantity only of the substance; and the perfect agreement with one another of numerous experiments made in this way, led me to place in it the greatest confidence. Facts, however, afterwards came to my knowledge, which proved that this action was not so absolutely uniform as had at first appeared; and although under the circumstances, and with the precautions (especially as to the relative quantities of the sub-

stances) which I have mentioned, the entire agreement of the experiments proves that the action is that which I have here given, yet this threw a certain doubt upon it, and it is only in some of my first experiments that I have used this plan of determining the oxygen uncontrolled by the following.

The determinations with platinum were made in a little apparatus of a very simple construction, which, as I shall elsewhere have occasion to mention it, I will call a bulb apparatus.



A is a small flask in which the weighed substance, together with a small portion of finely-divided platinum (prepared from platinum black by ignition) or of animal charcoal, which is equally effective, is placed. B is a glass bulb holding about two fluid ounces, which, before the experiment, is filled with dilute hydrochloric or acetic acid, and is closed by a well-ground stopper. C is a drying tube of potash. After weighing the apparatus, the stopper is loosened and the acid allowed to flow into the interior. The evolution of gas takes place immediately, but goes much slower than in the experiments with chromic acid. After eighteen or twenty hours the apparatus is again weighed, when the action may be considered terminated. It is, however, of course, to be weighed again until it ceases to lose weight. During the experiment a second potash tube, or a small tube dipping into a vessel of lime, is to be attached to the first, to prevent any increase of weight by absorption of moisture from the atmosphere. The following experiments were made in this manner:—

I. 2·389 grms. of the preparation A. gave a loss of 0·162 grm.

II. 2·437 grms. of the same gave a loss of 0·162 grm.

These experiments correspond to a loss per cent. of

I.	II.
6·78	6·64

III. 2·615 grms. of preparation B. gave a loss of 0·175 grm.

IV. 2·785 grms. of the same gave a loss of 0·184 grm.

These experiments correspond to a loss per cent. of

III.	IV.
6·63	6·60

These determinations entirely agree with each other; and the per-centage of oxygen in the substance is probably in fact (as is given by this experiment) a little less than that calculated from the amount of oxygen taken up, as in pulverizing it it is not possible to prevent the absorption of a little water by the baryta present, which must diminish the per-centage of oxygen. There is no violent rush of gas during the

experiment, nor is any variation of the action to be feared. I consider therefore this method to be as accurate as can be desired.

Experiments with Metallic Oxides.

The method of weighing the loss of oxygen, which succeeds very well for determining the amount of oxygen given off in the preceding experiments, cannot be employed with advantage for determining the amount given off by a metallic oxide in contact with the peroxide of barium. The evolution of gas is not rapid, continuing, at ordinary temperatures, sometimes for several days before all action ceases, during which time the apparatus is liable to alter in weight; and also more water is required to dissolve the baryta than can be introduced into the bulb of the apparatus, or conveniently and accurately be weighed. In these experiments, therefore, I determined indirectly the amount of oxygen given off by ascertaining the amount of metal reduced.

The form of the experiment was very simple. The weighed peroxide was intimately mixed in a flask with the metallic oxide, and a certain portion of water, about twelve ounces, poured upon the mixture. In the following experiments, those at the temperature of the air were placed in a cellar where the temperature was uniform, so that they might be comparable with one another, and the action was allowed to continue until all evolution of gas had ceased. In the experiments at 100° and at other temperatures, the water was first brought to the temperature required, then poured on the mixed substances and the mixture kept at the same temperature, either boiling or in a water-bath, during the action. In the experiments with oxide of silver, to determine the silver reduced, the residue, after the evolution of the gas had ceased, was treated with very dilute hydrochloric acid, with which it was allowed to remain in contact at least twelve hours. All oxide was thus converted into chloride. The fluid was now filtered from the residue and the hydrochloric acid washed out, the bulk of the solid substance being still kept in the flask in which the experiment was made. From this residue, consisting of chloride of silver and metallic silver, the silver was extracted by boiling with nitric acid, the substance on the filter being added to the rest and the filter also treated with acid. The solution was diluted and the silver dissolved, which was in fact the silver reduced, estimated as chloride. It is plain, that whether the oxide were reduced to metal or to a lower degree of oxidation, this silver must still be a correct measure of the oxygen lost. This method of determining the loss of oxygen I followed in all the experiments with silver compounds.

My first experiments were made before I had ascertained all the points necessary for the careful preparation of the peroxide, and the preparations used for these contained considerably less per-centage of oxygen than that which I afterwards readily procured, and contained also impurities from which the other preparations were free; in these experiments also the oxygen was determined only with bichromate of potash and hydrochloric acid. These circumstances in no way affect their general

result. But as the conclusions which they indicated were afterwards brought out and confirmed by experiments not open to these objections, it would be superfluous to give in their case also the numerical details of the determinations. As however they threw much light on the general nature of the inquiry, I cannot omit some account of them.

In the Tables which follow, I have arranged the chief results of these experiments. The column A. contains the amount of oxygen $=a$ in 100 parts of the peroxide of barium employed, as given by the determination with bichromate of potash. The column B. contains the relative loss of oxygen from the metallic oxide; the loss, that is, calculated on 100 parts of the peroxide of barium. This loss $=\psi$. The column C. contains the ratio of the quantity of oxygen in the peroxide of barium to the loss from the metallic oxide; the ratio, that is, of $a:\psi$ and the calculated value of ψ. In the column D. I have given the approximate ratio of the oxygen in the amount of peroxide of barium taken, to that in the oxide of silver or peroxide of lead taken in each experiment. The first Table contains the experiments made at 100° C. The first six experiments were made with oxide of silver, the rest with peroxide of lead. In the case of the peroxide of lead, the amount of oxygen lost by the peroxide was determined by extracting the residue after the experiment with very dilute nitric acid, which, leaving the peroxide, dissolves the oxide formed. The lead thus dissolved was estimated as sulphide.

Experiments at 100° C.

	A.	B.	C.		D.
1. 2.	4·03	1·65 1·64	5 : 2	1·61	3 : 2
3. 4.	4·18	1·95 2·08	2 : 1	2·09	3 : 2 1 : 1
5. 6.	5·85	3·08 2·99	2 : 1	2·92	AgO not weighed.
7. 8.	4·32	1·85 1·71	5 : 2	1·72	5 : 4 1 : 1
9. 10.	6·10	3·31 3·37	7 : 4	3·48	PbO_2 not weighed.

Classifying these ten experiments with reference to the ratios given in the third column, we find that they may be arranged thus:—

5 : 2, four experiments.
4 : 2, four experiments.
$3\frac{1}{2}$: 2, two experiments.

In the next Table the experiments were made below 100°; where the temperature is not given they were at the temperature of the air. The two last experiments were made with the peroxide of lead, the rest with the oxide of silver.

Experiments below 100°.

	A.	B.		C.		D.
1.	4·18	2·35	T. 38° to 42°.	7 : 4	2·38	3 : 1
2.		2·53				
3.		2·51	T. 24° to 26°.	5 : 3	2·50	5 : 2
4.		2·81		3 : 2	2·78	3 : 1
5.	4·32	2·93	T. 16°.	3 : 2	2·88	About 1 : 1 in the four experiments.
6.		3·00				
7.		*2·96	T. 0° upwards.	3 : 2		
8.		2·77				
9.	4·47	3·25		4 : 3	3·35	AgO not weighed.
10.		3·30				
11.	6·10	4·21		3 : 2	4·06	PbO_2 not weighed.
12.		3·93				

The experiments in this Table, arranged in the order of ratios, as those at the higher temperature, give the following series:—

$3\frac{1}{2}$: 2, one experiment.
5 : 3, two experiments.
3 : 2, seven experiments.
4 : 3, two experiments.

These experiments placed beyond doubt, that, under similar circumstances of temperature and mass, the loss of oxygen from the metallic oxide stood in a certain fixed relation to the quantity of the peroxide of barium employed. They showed also (speaking generally) that this loss varied inversely with the temperature, but yet it appeared that within certain limits (II. experiments 5, 6, 7, 8) the temperature might be very considerably altered without affecting the action. This was also the case, to a certain extent at any rate, with the mass; for a perfect agreement was found between experiments where the quantity of oxide of silver taken was considerably varied or even accidental. At the same time it was to be observed, that in determining these ratios a great deal would depend on the limits allowed for the error of analysis; and it was a question of great importance, and yet by no means easy to decide, whether they were absolutely such as I have here assumed them to be; that is to say, whether the difference between two nearly identical experiments was to be attributed to the error of analysis or to a real, though small, difference in the action. I determined therefore to make a more extended series of experiments, in which I might ob-

* The water in these two experiments was cooled down in ice before it was poured on the substances; at this low temperature no gas was given off. The action was allowed gradually to proceed as the temperature rose in the air.

serve the effect of varying the mass, at a constant temperature, and with the same preparation of the peroxide.

The great accuracy of the silver determination and the comparative facility of determining by it the loss of oxygen from the compounds of this metal, caused me to confine to them my attention. Indeed it was plain from experiments I had made with the oxide of mercury, as well as with peroxide of lead, that the general nature of the changes in question was, with any one of these substances, the same.

The following experiments were made with the chloride and the oxide of silver at 100°, and at the temperature of the air: I had already found how very greatly at the lower temperature this circumstance might be varied without alteration of the action; and in this case the experiments are arranged without any special reference to the slight variations of the temperature of the air. The peroxide taken is the same for each series; the general form of the experiments was precisely as already described.

Oxygen determinations.

The determinations of the oxygen in the different preparations of the peroxide of barium employed, gave the following results:—

I. Peroxide P.

I.—(1.) 2·8970 grms. of a peroxide (P) gave with hydrochloric acid and bichromate of potash, a total loss of 0·425 grm. of oxygen, corresponding to a loss of 14·67 per cent. on the peroxide.

(2.) 2·9215 grms. of the same substance gave, in a similar experiment, a total loss of 0·427 grm. of oxygen, corresponding to a loss of 14·61 per cent.

The oxygen in 100 parts of the peroxide, calculated from the above experiments, is,—

I.	II.
8·38	8·36.

(3.) 2·823 grms. of the same peroxide in an experiment with platinum and acetic acid, gave a loss of 0·235 grm., corresponding to a loss of 8·32 per cent. oxygen.

The mean of these three experiments gives 8·35 as the per-centage of oxygen in the substance.

II. Peroxide Q.

II.—(1.) 2·9565 grms. of a peroxide (Q) gave with hydrochloric acid and bichromate of potash, a total loss of 0·457 grm. of oxygen, corresponding to a loss of 15·45 per cent.

(2.) 2·9555 grms. of the same gave in a similar experiment, a total loss of 0·450 grm. of oxygen, corresponding to a loss of 15·22 per cent.

(3.) 2·955 grms. of the same gave with nitric acid and bichromate of potash, a total loss of 0·453 grm. of oxygen, corresponding to a loss of 15·32 per cent.

The oxygen in 100 parts of the peroxide, calculated from the above experiments, is,—

I.	II.	III.	Mean.
8·82	8·69	8·75	8·75

(1.) 2·6355 grms. of the peroxide gave with platinum and acetic acid, a total loss of 0·227 grm. of oxygen.

(2.) 2·9474 grms. of the same gave with platinum and acetic acid, a total loss of 0·257 grm. of oxygen.

(3.) 2·847 grms. of the same gave with platinum and hydrochloric acid, a total loss of 0·241 grm. of oxygen.

(4.) 2·9815 grms. of the same gave, in a similar experiment, a total loss of 0·254 grm. of oxygen.

These determinations correspond to a loss of oxygen per cent. of—

I.	II.	III.	IV.	Mean.
8·65	8·71	8·46	8·51	8·58

III. Peroxide O.

III.—(1.) 2·4875 grms. of a peroxide (O) gave with platinum and hydrochloric acid, a loss of 0·191 grm. of oxygen.

(2.) 2·515 grms. of the same, in a similar experiment, lost 0·191 grm. of oxygen.

(3.) 2·7296 grms. of the same, in a similar experiment, lost 0·204 grm. of oxygen.

These determinations correspond to a loss of oxygen per cent. of—

I.	II.	III.	Mean.
7·67	7·59	7·47	7·57

Experiments with Chloride of Silver at 100° C.

The following experiments were made with the peroxide P and chloride of silver at 100° C. The chloride of silver was in the finely-divided state in which it is produced by precipitating nitrate of silver with chloride of sodium. The precipitate with hydrochloric acid cannot so readily be mixed with the peroxide. The chloride of silver was dried either at 100° or at a gentle heat over a lamp; it was, when dried, in the state of a fine powder.

The following Table contains the details of the experiments:—

Table I.—A.

	Peroxide of barium P.	Chloride of silver taken.	Chloride of silver obtained.	Equivalent of oxygen.
	grms.	grms.	grms.	grms.
1.	3·0115	0·527	0·280	0·0155
2.	3·014	1·003	0·3945	0·0219
3.	3·0865	1·404	0·5633	0·0312
4.	3·0455	2·057	0·8085	0·0449
5.	3·0036	4·011	1·019	0·0566
6.	3·0206	5·963	1·0573	0·0587
7.	3·0295	7·983	1·1815	0·0656
8.	2·958	9·235	1·087	0·0605
9.	2·967	11·139	1·170	0·0652
10.	3·0465	11·064	1·3105	0·0728
11.	3·0375	15·960	1·3515	0·0759
12.	3·0695	19·920	1·3425	0·0745
13.	3·0125	8·059	1·4795	0·0822

In the second Table, B, which follows, the oxygen equivalent to the reduced silver is compared with the oxygen in the peroxide; the peroxide being taken as 100, and the oxygen therefore as 8·34. In the third Table, the oxygen in the peroxide is taken as the unit. The third and fourth columns in both cases contain the assumed and calculated ratio of the oxygen lost by the peroxide to that equivalent to the reduced silver. I have assumed as this ratio the simplest ratio which agrees with the experiments, as a convenient and sufficiently accurate expression of the loss.

TABLE I.—B.

	Oxygen in the peroxide of barium $P=a$.	Oxygen equivalent to the chloride of silver reduced $=\psi$.	Ratio, $a:\psi$.	Calculated ratio.
1.		0·51		
2.		0·72		
3.		1·01		
4.		1·47		
5.		1·88	9 : 2	1·85
6.		1·94		
7.	8·34	2·18		
8.		2·04	4 : 1	2·08
9.		2·19		
10.		2·42		
11.		2·47	7 : 2	2·38
12.		2·42		
13.		2·73	3 : 1	2·78

TABLE I.—C*.

	Oxygen in the peroxide of barium $=a$.	Oxygen equivalent to the chloride of silver reduced $=\psi$.	Ratio, $a:\psi$.	Calculated ratio.
1.		6·11		
2.		8·63		
3.		12·11		
4.		17·62		
5.		22·54	9 : 2	22·22
6.		23·26		
7.	100	26·13		
8.		24·46	4 : 1	25·0
9.		26·25		
10.		29·01		
11.		29·61	7 : 2	28·57
12.		29·01		
13.		32·73	3 : 1	33·33

* In these Tables the experiments are arranged in all cases according to the nature of the actions, and not with reference to the quantities taken of the decomposed bodies. But for the sake of a ready general compa-

100 parts of this peroxide require 149·7 parts of chloride of silver to one equivalent of the oxygen it contains. Hence 3 grms. of the peroxide require 4·491 grms. of the chloride for the same proportion.

In the first four experiments, in which comparatively small quantities of chloride of silver, at most not half an equivalent, were taken, the loss increases nearly with the mass of the chloride, and bears therefore no constant ratio to the loss from the peroxide. In all these four experiments the chloride has been reduced nearly in the same proportion, but yet between the first and second experiment there is a difference which is not found between the other three, as may be seen from the following comparison of the chloride of silver taken with the chloride found.

Exp.	Chloride of silver taken.	Chloride of silver found.
1.	100	53·1
2.	100	39·3
3.	100	40·1
4.	100	39·3

It appears from this comparison that in the three last of these experiments exactly two-fifths of the chloride taken are reduced, and we may regard this limit of reduction as the circumstance which here determines the action. The gradual increase of loss, with the mass, does not continue, or the increase becomes very small, for one and three equivalents of chloride give very nearly the same amount of reduced silver, equivalent to exactly one-fourth of the oxygen in the peroxide. There is also a constant ratio of loss, which appears likewise to be connected with the increase of mass where the ratio is as 7 : 2, and there is one exception to the order of the series where the loss does not stand in the same general relation to the mass, which may be observed in the other experiments. In this, however, the same simplicity of ratio prevails, and it is evidently a term of the series; the ratio of the loss being as 3 : 1. It is worthy of observation, that the turning-point of the action where the loss ceases to increase with the mass, lies at any rate near to that point where the decomposing bodies are taken in equal equivalent proportions.

My experiments had led me to suspect that some circumstance connected with the particular preparation of the peroxide employed materially influenced the results. This circumstance might be the proportion of free baryta in the peroxide, which was not quite the same in different preparations, or it might be some peculiarity in the molecular condition of the peroxide itself due to some other cause; I repeated therefore the experiments made with one peroxide with another preparation, and arranged these experiments apart.

The following experiments were made also with chloride of silver at 100°, but with the peroxide Q containing 8·58 per cent. of oxygen. The Tables are of the same nature as before.

rison of these quantities, nearly the same quantity of the peroxide, 3 grms., was, with some few exceptions, always employed. The experiments, as will be seen, do not call for any more exact comparison than can thus at a glance be made.

Table II.—A.

	Peroxide of barium Q.	Chloride of silver taken.	Chloride of silver obtained.	Equivalent of oxygen.
1.	3·0065 grms.	4·0015 grms.	0·5305 grms.	0·0295 grms.
2.	2·971	5·003	0·709	0·03952
3.	2·9995	8·0015	0·732	0·0408
4.	3·0145	8·0745	0·9845	0·0548
5.	2·962	10·129	0·968	0·05396
6.	3·001	11·9955	1·003	0·05591
7.	2·985	14·936	1·126	0·0627
8.	2·9545	12·0175	1·2245	0·06826
9.	2·9965	16·0105	1·3205	0·07361

Table II.—B.

	Oxygen in the peroxide of barium $Q=a$.	Oxygen equivalent to the chloride of silver reduced $=\psi$.	Ratio, $a:\psi$.	Calculated ratio.
1.		0·96	9 : 1	0·95
2.		1·33	6 : 1	1·43
3.		1·36		
4.		1·81		
5.	8·58	1·82	9 : 2	1·90
6.		1·86		
7.		2·10	4 : 1	2·14
8.		2·31	7 : 2	2·45
9.		2·45		

Table II.—C.

	Oxygen in the peroxide of barium $Q=a$.	Oxygen equivalent to the chloride of silver reduced $=\psi$.	Ratio, $a:\psi$.	Calculated ratio.
1.		11·18	9 : 1	11·11
2.		15·5	6 : 1	16·6
3.		15·8		
4.		21·0		
5.	100	21·2	9 : 2	22·22
6.		21·6		
7.		24·4	4 : 1	25·00
8.		26·9	7 : 2	28·57
9.		28·5		

3 grms. of this peroxide require 4 grms. of chloride of silver as equivalent to the oxygen it contains. Thus the experiments from 1 to 6 in this series, were made with a proportion of the chloride, on the whole greater than the experiments 5 to 9 on the first Table. Yet a great diminution is to be observed in the loss of oxygen; in experi-

ment 1 only 13·2 parts out of 100 of the chloride are reduced. And here the ratio 9 : 2 occupies the place of the ratio 4 : 1 or 8 : 2 on the other series. But the limiting ratio of 7 : 2 is in both series the same, and on the whole a certain increase of loss, although not a gradual increase, is to be observed with the increase of the chloride taken. These experiments confirm the fact, that under similar circumstances the different preparations of the peroxide have a different reducing power.

Experiments with Chloride of Silver at the temperature of the air.

The next experiments were made also with the chloride of silver, but at a lower temperature, the temperature of the air. I had already found how very much at this low temperature the temperature might be varied without alteration of the action, and in this case the experiments are arranged without any special reference to the variation of the temperature. The peroxide in the first series was the same as that taken in the last experiments, namely, the peroxide Q containing 8·58 per cent. of oxygen.

TABLE III.—A.

	Peroxide of barium Q.	Chloride of silver taken.	Chloride of silver obtained.	Equivalent of oxygen.
1.	3·034 grms.	4·0125 grms.	1·366 grms.	0·076 grms.
2.	2·9942	4·988	1·480	0·0825
3.	3·0275	6·1315	1·545	0·08613
4.	2·994	8·0905	1·9415	0·10823
5.	2·9742	10·016	2·043	0·1138
6.	2·9532	14·916	2·019	0·1125
7.	3·014	9·9915	2·336	0·1302
8.	2·9915	12·9075	2·3125	0·1289
9.	2·0132	14·916	1·5485	0·0863

TABLE III.—B.

	Oxygen in the peroxide of barium Q=a.	Oxygen equivalent to the chloride of silver reduced=ψ.	Ratio, $a:\psi$.	Calculated ratio.
1.	8·58	2·50	7 : 2	2·48
2.		2·75	3 : 1	2·86
3.		2·84		
4.		3·61	7 : 3	3·67
5.		3·82	9 : 4	3·81
6.		3·80		
7.		4·31	2 : 1	4·29
8.		4·30		
9.		4·28		

TABLE III.—C.

	Oxygen in the peroxide of barium Q $=a$.	Oxygen equivalent to the chloride of silver reduced $=\psi$.	Ratio, $a:\psi$.	Calculated ratio.
1.	100	29·13	7 : 2	28·57
2.		32·05	3 : 1	33·33
3.		33·10		
4.		42·07	7 : 3	42·85
5.		44·52	9 : 4	44·44
6.		44·28		
7.		50·23	2 : 1	50·0
8.		50·11		
9.		49·88		

The point to be observed in these experiments is the great increase of reduction at the lower temperature. The comparative experiments in this and the last series, show that from corresponding quantities of the chloride, as nearly as possible twice the amount of silver is reduced; and these experiments, it is worthy of remark, take up the action exactly at the point where the other series terminates, so that the expression of the relative loss forms a continuation of the series of ratios commencing with 7 : 2 and terminating with 2 : 1.

The following are a few experiments made with the peroxide P, containing 8·34 per cent. of oxygen.

TABLE IV.—A.

	Peroxide of barium Q.	Chloride of silver taken.	Chloride of silver obtained.	Equivalent of oxygen.
1.	3·020 grms.	1·012 grms.	0·5715 grms.	0·03175 grms.
2.	3·032	2·009	0·765	0·0426
3.	3·0256	3·895	1·484	0·08244
4.	3·0005	8·879	1·733	0·0962
5.	3·0046	6·11	1·9495	0·1083
6.	3·05	11·983	2·065	0·1147

TABLE IV.—B.

	Oxygen in the peroxide of barium P $=a$.	Oxygen equivalent to the choride of silver reduced $=\psi$.	Ratio, $a:\psi$.	Calculated ratio.
1.	8·34	1·04	8 : 1	1·04
2.		1·40	6 : 1	1·39
3.		2·72	3 : 1	2·78
4.		3·26	5 : 2	3·33
5.		3·60	9 : 4	3·70
6.		3·72		

TABLE IV.—C.

	Oxygen in the peroxide of barium P$=a$.	Oxygen equivalent to the chloride of silver reduced$=\psi$.	Ratio, $a:\psi$.	Calculated ratio.
1.	100	12·47	8 : 1	12·5
2.		16·06	6 : 1	16·66
3.		32·61	3 : 1	33·33
4.		39·08	5 : 2	40·0
5.		43·16	9 : 4	44·44
6.		44·60		

The experiments with this peroxide give about the same range of action as with the last. On the whole, however, the loss here, as at 100° with the same substance, is rather less, but the difference is not so apparent.

Experiments with the Oxide of Silver at 100° C.

The following are experiments with the oxide of silver at 100° C. The oxide was prepared either by precipitation with baryta water or with a pure potash. It contained no chloride but some carbonate, and was dried at 100°. The peroxide employed was the peroxide P, containing 8·34 per cent. of oxygen; 3·63 grms. of the oxide of silver are equivalent to 3 grms. of the peroxide.

TABLE V.—A.

	Peroxide of barium P.	Oxide of silver.	Chloride of silver found.	Equivalent of oxygen.
1.	3·0225 grms.	0·855 grms.	0·625 grms.	0·0347 grms.
2.	3·0295	1·525	0·8353	0·0463
3.	2·9807	1·205	0·9784	0·0543
4.	3·006	1·832	1·165	0·0647
5.	3·0107	2·235	1·369	0·0760
6.	2·997	2·920	1·5565	0·0864
7.	2·982	4·692	1·492	0·0831
8.	3·007	4·890	1·510	0·0841
9.	3·0185	6·182	1·483	0·08238
10.	3·601	6·266	1·874	0·1041
11.	2·986	6·4675	1·503	0·0837
12.	3·067	9·339	1·6345	0·0908
13.	3·019	11·051	1·7325	0·09625
14.	3·0485	7·810	1·7785	0·0988
15.	2·983	4·932	1·84	0·1025
16.	3·616	15·675	2·395	0·133
17.	2·9725	9·5345	2·001	0·1115
18.	3·0075	12·2035	2·2365	0·1248

TABLE V.—B.

	Oxygen in the peroxide of barium P = a.	Oxygen of the oxide of silver reduced = ψ.	Ratio, $a : \psi$.	Calculated ratio.
1.		1·14		
2.		1·52	5 : 1	1·67
3.		1·82		
4.		2·15	4 : 1	2·08
5.		2·52	7 : 2	2·38
6.		2·88		
7.		2·78		
8.		2·79		
9.	8·34	2·72	3 : 1	2·78
10.		2·88		
11.		2·80		
12.		2·96		
13.		3·18		
14.		3·24	5 : 2	3·33
15.		3·43		
16.		3·67	9 : 4	3·70
17.		3·75		
18.		4·14	2 : 1	4·17

TABLE V.—C.

	Oxygen in the peroxide of barium P = a.	Oxygen of the oxide of silver reduced = ψ.	Ratio, $a : \psi$.	Calculated ratio.
1.		13·66		
2.		18·22	5 : 1	20·0
3.		21·82		
4.		25·77	4 : 1	25·0
5.		30·21	7 : 2	28·57
6.		34·53		
7.		33·33		
8.		33·45		
9.		32·61	3 : 1	33·33
10.	100	34·53		
11.		33·57		
12.		35·49		
13.		38·12		
14.		38·84	5 : 2	40·00
15.		41·12		
16.		44·00	9 : 4	44·44
17.		44·84		
18.		49·63	2 : 1	50·00

These experiments give the same results as those made with the chloride of silver at the lower temperature, and comprise as these a series of ratios beginning with 7 : 2 and ending with 2 : 1. The experiments with the smaller quantities of oxide show

also the same kind of progressive increase of loss, as already observed with the chloride; the increase however is not so constant. In experiments 4 and 5 exactly half the oxide is reduced; the ratio of the oxygen in the oxide of silver taken, to the oxygen from the oxide reduced, being in the two experiments as 100 : 51·2 and 100 : 49·31; the presence however of carbonate of silver in the oxide renders this fact less certain than the similar fact observed in the case of the chloride of silver (Table I.).

I repeated these experiments with another preparation of the peroxide, the peroxide O, containing 7·57 per cent. of oxygen; 3·12 grms. of oxide of silver are equivalent to 3 grms. of this peroxide.

TABLE VI.—A.

	Peroxide of barium O.	Oxide of silver.	Chloride of silver obtained.	Equivalent of oxygen.
1.	3·0666 grms.	2·737 grms.	1·692 grms.	0·094 grms.
2.	3·006	3·659	1·7146	0·0952
3.	3·098	4·801	1·7335	0·0963
4.	3·007	5·426	2·0735	0·1151
5.	3·0806	11·592	2·5123	0·1395

TABLE VI.—B.

	Oxygen in the peroxide of barium O $=a$.	Oxygen of the oxide of silver reduced $=\psi$.	Ratio, $a:\psi$.	Calculated ratio.
1.		3·09		
2.		3·16	5 : 2	3·02
3.	7·57	3·10		
4.		3·85	2 : 1	37·8
5.		4·52	5 : 3	4·74

TABLE VI.—C.

	Oxygen in the peroxide of barium O $=a$.	Oxygen of the oxide of silver reduced $=\psi$.	Ratio, $a:\psi$.	Calculated ratio.
1.		40·81		
2.		40·74	5 : 2	40·00
3.	100	40·95		
4.		50·59	2 : 1	50·00
5.		59·70	7 : 3	60·00

The experiments 1, 2, 3 here correspond to the experiments 6, 7, 8, 9 in Table V.; they give however a considerably greater loss, the ratio being 5 : 2 instead of 3 : 1. This difference, it is probable, extends also to the higher terms in the series, for we

have here a ratio 5 : 3, which is a greater loss than any in the other series of experiments. It is worthy of remark, that the loss per cent. on the peroxide is nearly the same in the two, which might lead us to think that this loss stood in some fixed ratio to the baryta of the substance, with the whole of which the oxygen of the peroxide may be considered to be in combination. This however is doubtless but a coincidence, as the experiments with chloride of silver, made with different preparations of the peroxide, where similar differences exist, do not show this relation.

Experiments with the Oxide of Silver at the temperature of the air.

The following experiments were made with the peroxide P (containing 8·34 per cent. of oxygen) and oxide of silver at the temperature of the air.

TABLE VII.—A.

	Peroxide of barium P.	Oxide of silver.	Chloride of silver found.	Equivalent of oxygen.
1.	2·999 grms.	0·824 grms.	0·528 grms.	0·2293 grms.
2.	3·004	1·604	0·9135	0·05075
3.	3·017	3·123	1·3915	0·0773
4.	3·022	3·994	1·6815	0·0934
5.	3·039	6·313	1·990	0·1105
6.	3·04	7·788	2·057	0·1142
7.	3·029	9·400	2·041	0·1133
8.	2·9417	2·964	2·2055	0·1225
9.	3·059	15·720	2·3785	0·132
10.	15·925	26·522	13·677	0·759
11.	3·478	9·405	2·965	0·1647
12.	3·021	7·6195	3·222	0·1796

TABLE VII.—B.

	Oxygen in the peroxide of barium P = a.	Oxygen of the oxide of silver reduced = ψ.	Ratio, $a : \psi$.	Calculated ratio.
1.		0·97		
2.		1·68		
3.		2·56	7 : 2	2·38
4.		3·10	5 : 2	3·33
5.		3·63		
6.	8·34	3·75	9 : 4	3·70
7.		3·74		
8.		4·16	2 : 1	4·17
9.		4·31		
10.		4·76	7 : 4	4·76
11.		4·70		
12.		5·94	7 : 5	5·95

Table VII.—C.

	Oxygen in the peroxide of barium P $=a$.	Oxygen of the oxide of silver reduced $=\psi$.	Ratio, $a:\psi$.	Calculated ratio.
1.	100	11·63		
2.		20·14		
3.		30·69	7 : 2	28·57
4.		37·17	5 : 2	40·0
5.		43·52	9 : 4	44·44
6.		44·96		
7.		44·84		
8.		49·88	2 : 1	50·00
9.		51·67		
10.		57·07	7 : 4	57·1
11.		56·35		
12.		71·22	7 : 5	71·42

When small quantities of the oxide of silver are taken, the loss is not very different from that at the higher temperature, as is also the case in the experiments with the chloride; but after a certain point the actions diverge, and the total general result gives an entirely different range of action in the two series. In all cases, after a certain point, the mass ceases to have a determinate influence on the action; and here this influence would seem soon to be entirely lost, for after the first two or three experiments, no relation whatever can be traced between the relative masses of the substances and the proportion of reduced silver. At the same time, even these experiments, which we may regard as accidental, arrange themselves in a certain order, and give on the whole higher numbers in the series of ratios than any yet obtained. This series may be extended yet further; thus two experiments with peroxide O, at the temperature of the air, gave—

Table VIII.—A.

	Peroxide of barium O.	Oxide of silver.	Chloride found.	Equivalent of oxygen.
1.	2·926 grms.	5·186 grms.	2·8557 grms.	0·1586 grm.
2.	3·06	5·064	3·0402	0·1689

Table VIII.—B.

	Oxygen in the peroxide of barium O $=a$.	Oxygen of the oxide of silver reduced $=\psi$.	Ratio, $a:\psi$.	Calculated ratio.
1.	7·57	5·42	7 : 5	5·40
2.		5·51		

TABLE VIII.—C.

	Oxygen in the peroxide of barium O = a.	Oxygen of the oxide of silver reduced = ψ.	Ratio, $a : \psi$.	Calculated ratio.
1. 2.	100	71·59 72·78	7 : 5	71·42

These experiments, although made with but small quantities of the oxide, give a loss as great as any made with the other preparation.

Two experiments with the peroxide Q, at the same temperature, gave a yet greater loss.

TABLE IX.—A.

	Peroxide of barium Q.	Oxide of silver.	Chloride of silver found.	Equivalent of oxygen.
1.	2·985 grms.	7·878 grms.	3·843 grms.	0·2142 grm.
2.	2·9544	7·9215	3·801	0·2119

TABLE IX.—B.

	Oxygen in the peroxide of barium Q = a.	Oxygen of the oxide of silver reduced = ψ.	Ratio, $a : \psi$.	Calculated ratio.
1. 2.	8·58	7·17 7·17	6 : 5	7·15

TABLE IX.—C.

	Oxygen in the peroxide of barium Q = a.	Oxygen of the oxide of silver reduced = ψ.	Ratio, $a : \psi$.	Calculated ratio.
1. 2.	100	83·56 83·56	6 : 5	83·33

This is the greatest amount of loss which I have yet obtained in these experiments with silver compounds, which has never quite equaled the oxygen in the peroxide.

The specific difference in the amount of reduction of the chloride and of the oxide of silver under otherwise similar circumstances with the same preparation of the peroxide, that is, at the same temperature, depends doubtless on the difference in the chemical nature of the substances. It was an interesting matter of inquiry whether this difference would be found with other silver compounds: I have not yet extended my experiments in this direction so far as the importance of the question demands, but the following results show both the identity and the difference which may exist in the reaction.

The following experiments were made at 100° C. with carbonate of silver and with

the peroxide Q, which was used also in the experiments with the chloride (Table II.). Two equivalents of the carbonate were taken to one of the peroxide.

Table X.—A.

	Peroxide of barium Q.	Carbonate of silver.	Chloride of silver found.	Equivalent of oxygen.
1.	3·025 grms.	9·2055 grms.	1·339 grm.	0·0746 grm.
2.	3·03	9·2085	1·490	0·0830

Table X.—B.

	Oxygen in the peroxide of barium Q $=a$.	Oxygen of the carbonate of silver reduced $=\psi$.	Ratio, $a:\psi$.	Calculated ratio.
1.	8·58	2·46	7 : 2	2·45
2.		2·73	3 : 1	2·86

Table X.—C.

	Oxygen in the peroxide of barium Q $=a$.	Oxygen of the carbonate of silver reduced $=\psi$.	Ratio, $a:\psi$.	Calculated ratio.
1.	100	28·67	7 : 2	28·57
2.		31·81	3 : 1	33·3

Two other experiments were made with the same substance at a lower temperature, 17° C.

Table XI.—A.

	Peroxide of barium Q.	Carbonate of silver.	Chloride of silver found.	Equivalent of oxygen.
1.	2·926 grms.	9·2075 grms.	1·714 grm.	0·95556 grm.
2.	3·012	9·1525	1·938	0·108

Table XI.—B.

	Oxygen in the peroxide of barium Q $=a$.	Oxygen of the carbonate of silver reduced $=\psi$.	Ratio, $a:\psi$.	Calculated ratio.
1.	8·58	3·26	5 : 2	3·43
2.		3·58		

Table XI.—C.

	Oxygen in the peroxide of barium Q $=a$.	Oxygen of the carbonate of silver reduced $=\psi$.	Ratio, $a:\psi$.	Calculated ratio.
1.	100	37·99	5 : 2	40
2.		41·72		

These two experiments were made in the small bulb-apparatus used for the oxygen determinations, and thus the total loss of oxygen was estimated as well as the reduced silver. The action proceeds more rapidly than in the experiments with the chloride and oxide, so as to render it probable that a more accurate result might in this manner be obtained with the carbonate than with those substances. In the first experiment the total loss was 12·19 per cent.; in the second, 11·91 per cent. The sum of the oxygen in the peroxide and that due to the silver reduced, as given by the determinations, is in the first experiment 11·84 per cent.; in the second, 12·16 per cent.; which so agree with the other numbers as to show that no oxygen is retained by the substances.

On turning to those experiments with the chloride of silver at 100° C. and at the lower temperature, with which these experiments are comparable (Tables I. and II.), it will be seen that the reduction is nearly the same with the two substances.

With sulphate of silver the result was very different. The two following experiments were made with pure crystallized sulphate of silver and the peroxide Q, at 100° C. In the first experiment one equivalent, in the second two equivalents of the sulphate were taken.

Table XII.—A.

	Peroxide of barium Q.	Sulphate of silver.	Chloride of silver found.	Equivalent of oxygen.
1.	2·969 grms.	5·449 grms.	0·118 grm.	0·00657 grm.
2.	3·005	10·805	0·542	0·03021

Table XII.—B.

	Oxygen in the peroxide of barium Q $=a$.	Oxygen of the sulphate of silver reduced $=\psi$.	Ratio, $a:\psi$.	Calculated ratio.
1.	8·58	0·221	40 : 1	0·21
2.		1·00	9 : 1	0·95

Table XII.—C.

	Oxygen in the peroxide of barium Q $=a$.	Oxygen of the sulphate of silver reduced $=\psi$.	Ratio, $a:\psi$.	Calculated ratio.
1.	100	2·57	40 : 1	2·5
2.		11·66	9 : 1	11·1

The amount of reduction is here so small that the action of the sulphate of silver is very nearly the same as the so-called contact action of platinum. I have already pointed out that the action of very small quantities of the chloride and of the oxide of silver is also of the same nature. In the case of these different chemical substances, therefore, it approaches the same limit, although according to a different law.

I have now brought this investigation to that point at which for the present I shall leave it. I would willingly have attempted to render these tables of experiments more complete, had it not appeared to me that there were certain defects in the method of experimenting which rendered this course unadvisable. One most important question is, whether the series of ratios by which I have expressed the relative loss of oxygen from the two substances is truly an intermittent or a continuous series, that is to say, whether there are or are not certain points where this ratio is constant although the proportions of the masses are varied. That there is with each chemical substance at least one such point, namely, a certain limit of reduction beyond which a great increase of the mass of the substance to be reduced does not alter the action, may, I think, be asserted with confidence, and without in any way implying that all the ratios which these experiments have brought to light are of this nature; yet it is difficult to account for the great coincidence of experiments made with very different proportions of the substances, without admitting a tendency of the action to fall into certain ratios rather than into others. Indeed the experiments appear to me to indicate both that for certain intervals the loss of oxygen truly does vary directly with the mass of the substance reduced, and that in certain other points the mass may be varied and the loss yet be constant. In these experiments, however, I could never secure that perfect agreement between two experiments made under exactly similar circumstances, by which alone I could hope to answer a question demanding such exactness. One principal reason of the anomalies which the experiments occasionally exhibit is doubtless, that by simply mixing the substances, even where the same quantities are taken in two experiments, the same conditions of mass are yet not realized: I therefore turned my attention to other methods of experimenting, by which it is my hope to answer this question in a more exact and satisfactory manner. My experiments are not yet complete, but I may mention, that by operating with solutions, I have obviated this difficulty. Lastly, let me thus sum up the general results of these experiments. First, the amount of oxygen lost by the substance reduced is, under circumstances otherwise similar, in a definite and constant ratio to the quantity of the peroxide of barium employed. Secondly, this loss is greater as the mass of the substance reduced is increased, and diminishes as the temperature at which the reduction takes place is raised. It varies also with the preparation of the peroxide. Thirdly, in each series of experiments there is a certain definite limit of reduction beyond which at any rate a very great increase of the mass of the substance reduced causes no increase of the loss of oxygen*. Lastly, in reference to that chemical question from which this inquiry proceeded, namely, how much oxygen is lost by the substance reduced in proportion to the loss of oxygen from the peroxide of barium, it is to be observed, that however much the circumstances are varied, there are yet two limiting

* It appears from other experiments which I have made, that with each chemical substance there is a specific limit of reduction of this kind; thus, for example, in the experiment with chromic acid (p. 779), the only reason of the constant reaction there obtained, is that by taking a very great excess of the bichromate of potash,

ratios between which the whole action is comprised, either of which may be almost indefinitely approached. These are the limit of least reduction, in which the ratio of the loss from the peroxide of barium to that from the metallic oxide is infinite, or as 1 : 0; and the limit of greatest reduction, which is the ratio of equality, in which the two substances would lose an equal amount of oxygen. This limit also, in no one experiment with any silver compound, have I ever exceeded or reached. The first limit is that in which the action would be a pure reduction by contact, such as takes place when platinum or carbon are the substances which cause the decomposition. The other would be a purely chemical action, such as may be seen in an experiment to which I will now proceed, and which, although perhaps not at first sight as striking as the reduction of the metallic oxides, is, philosophically considered, quite as remarkable, being indeed the same experiment, but detached from circumstances which give in the other case the apparent differences to the reaction.

Action of Iodine on the Peroxide of Barium.

It occurred to me, that if it were for the reasons I have stated, that the iodide and chloride of silver decompose the peroxide of barium with the evolution of the oxygen it contains, iodine and chlorine should produce a similar effect. Indeed this was a very critical and important experiment; for we know the action of chlorine and iodine on baryta; and on the view which is usually taken of this decomposition and of other analogous changes, namely, that the iodine takes away the barium from the oxygen because of its superior affinity for the metal, and that the oxygen which is thus liberated combines with the iodine because it is in a nascent condition, and thus converts it into iodous or iodic acid; by acting on iodine with the peroxide of barium, we ought to have just twice as much iodic acid formed as in the other case; nor was there any apparent reason why the oxygen from the peroxide of barium should not oxidize as well as the oxygen from the baryta. The same iodine, the same barium, and the same oxygen are supposed to be present; and if the iodine acted at all on the peroxide, the oxygen would still be nascent. Considered however from that theoretical point of view which I have given in the early part of this paper, there was no reason to expect this result. I have there suggested (p. 767), that in the action of iodine upon baryta, the combination of iodine and oxygen takes place solely on account of the polar relation in which the particles are placed under the peculiar circumstances of the action. Each particle in the change being alternately positive and negative, thus:—

$$\underbrace{\overset{+}{\mathrm{I}}\,\overset{-}{\mathrm{I}}\,\overset{+}{\mathrm{Ba}}\overset{-}{\mathrm{O}}}=\mathrm{IBa}+\mathrm{IO}.$$

I at once determined the action to a limit which it could not exceed. When small quantities of the bichromate are employed the result is entirely different, and a very small quantity of the bichromate decomposes a very great excess of the peroxide. The reaction which I have given (p. 769) is to a certain extent hypothetical, it is the limit of greatest reduction.

When phosphorus and iodine are used instead of iodine in this experiment, no essential change has taken place in the causes which determine the combining condition of the particles, but a particle of phosphorus now stands in the same relation to the baryta as the particle of iodine in the other experiment, thus:—

$$\underbrace{\overset{+}{\mathrm{P}}\ \overset{-}{\mathrm{I}}\,\overset{+}{\mathrm{Ba}}\overset{-}{\mathrm{O}}}=\mathrm{IBa}+\mathrm{PO}.$$

Now if thus intercalating the particle of phosphorus transfers the action from the iodine to the phosphorus, so also intercalating a particle of oxygen might transfer the action from the iodine to the oxygen itself, which would now be the truly oxidized body, provided of course that the particle of oxygen thus intercalated were a body which stood to the other particles with which it was in contact, in the same chemical relation as the iodine and phosphorus in the other changes; nor do I see that this substitution of the oxygen for the iodine is more truly extraordinary than the substitution of the iodine for the phosphorus. Indeed, if we inquire into the causes of chemical change, the two would depend essentially upon one and the same fact, namely, a chemical difference between the particles of the element. In the one case we have the chemical division of the element, in the other the chemical synthesis to explain; and to give a philosophical account of either fact we must assume alike the existence of a chemical difference between its particles. Now, when we substitute peroxide of barium for baryta in the iodine experiment, this very intercalation of the oxygen has been effected, and the conditions of the change been fulfilled, the polar cycle being completed, thus:—

$$\underbrace{\overset{-}{\mathrm{I}}\ \overset{+}{\mathrm{Ba}}\overset{-}{\mathrm{O}}\ \overset{+}{\mathrm{O}}}=\mathrm{IBa}+\mathrm{O}_2.$$

In fact, when water is poured upon a mixture of peroxide of barium and iodine, a violent evolution of gas occurs, and the same when chlorine is led into water containing the peroxide, or when the peroxide is thrown into a solution of hypochlorite of lime in acetic acid.

This experiment with iodine is so important, that I shall give at full length the determinations of the quantity of gas evolved in this reaction. The experiment was made in the small bulb-apparatus already described, p. 779.

The weighed peroxide and weighed iodine were mixed in the flask, the bulb being filled with distilled water; the apparatus was weighed, and the water then allowed to descend on the mixture. The loss on again weighing the apparatus is the oxygen evolved. The same precautions are to be taken in the experiment as in the oxygen determination.

The peroxide used in the following experiments was the peroxide Q, containing 8·58 per cent. of oxygen; 100 parts of this peroxide require 138 parts of iodine as one equivalent to the oxygen it contains. The first of the following Tables contains

the quantities of the substances taken and the loss; in the second the comparison is made between this loss and the oxygen of the peroxide.

TABLE XIII.—A.

	Peroxide of barium Q.	Iodine.	Loss of oxygen.
1.	1·094 grms.	30·242 grms.	0·187 grm.
2.	0·973	16·082	0·164
3.	0·843	11·633	0·140
4.	1·409	15·5485	0·238
5.	1·845	17·8225	0·315
6.	2·0675	17·130	0·358
7.	0·7995	5·5325	0·140
8.	1·9364	10·6495	0·331
9.	1·2405	5·277	0·212
10.	1·275	3·517	0·215

TABLE XIII.—B.

	Oxygen in the peroxide Q.	Loss of oxygen.	Oxygen in the peroxide.	Loss of oxygen.
1.		17·09		199·1
2.		16·85		196·3
3.		16·60		193·4
4.		16·89		196·8
5.		17·06		198·8
6.	8·58	17·31	100	201·7
7.		17·51		204·0
8.		17·09		199·1
9.		17·08		199·0
10.		16·86		196·5

The mean of these experiments gives the ratio of the oxygen in the peroxide compared with the loss, as 8·58 : 17·03, or as 100 : 198·4. They clearly prove that the reaction is as I have stated. The quantity of iodine taken varies from 2 to 20 equivalents. The number of these experiments may appear superfluous, but there were some circumstances connected with the reaction when a smaller quantity of iodine was employed, which caused me particularly to inquire whether any excess of iodine would alter its nature. It is plain that this cannot be done. I have also ascertained the fact, that with a perfectly pure peroxide an equivalent of iodine always decomposes exactly an equivalent of the peroxide, so that if an excess of the peroxide be taken it remains undecomposed. In this important point this reaction differs from the other experiments I have given, in which very small quantities of the substance decompose the *whole* of the peroxide present. With iodine this will not take place.

The decomposition of the chloride of silver by the peroxide of barium is a true link between these experiments with iodine and the reduction of the metallic oxides. In whatever rational form we may express these facts, the facts themselves are the same. We cannot *see* the mode in which the action is effected, nor for the present argument is it at all important whether we consider, as we reasonably may, that the

change takes place* by the decomposition of water, and that the oxygen which is formed is the result of the combination of the element of the water with the element of the peroxide, or whether we consider the iodine to be transferred directly to the barium, and the whole of the oxygen to come from the peroxide itself. Whatever theory accounts for this reaction, the same theory, I will venture to assert, will explain the decomposition of the metallic oxides. It remains only to show why it is that this decomposition with iodine comes before us as a chemical reaction of the simplest nature, and that in the other experiments the decomposition is apparently so variable. The reason I believe to be this, that in these latter experiments the peroxide is simultaneously decomposed in two ways, between which we must discriminate, by the action of contact and by the chemical action of the oxide or chloride. The decomposition by platinum is a pure contact action, in which the peroxide loses only one equivalent of oxygen. The decomposition with iodine is a pure chemical action, in which two equivalents of oxygen are given off. The action with metallic oxides is an action compounded of these two, and therefore it is that the loss, as I have already pointed out, ever lies between these two limits. There are two causes by either or by both of which this decomposition may be effected; the one, the metallic silver or other substance which is the result of the reduction; the other, the very oxide or chloride or peroxide itself which is reduced. Certain oxides which are not themselves reduced, can unquestionably act in this manner; and it is highly probable therefore that those which are reduced, and which belong to the same class of bodies, have the same property. On this view therefore the law of the formation of the oxygen is ever one and the same, and so far as relates to the chemical action of the peroxide of barium on the metallic oxide this is ever definite. The fact therefore which is expressed by the series of ratios is by no means any different forms of combination of the particles of the oxygen with each other, but simply the way in which the decomposition of the peroxide of barium is distributed between these different modes of action, and the relative velocity with which these two modes of decomposition take place. If, for example, the ratio of the loss of oxygen from the peroxide of barium to that from the metallic oxide, be as 4 : 1, three parts of the peroxide of barium will have been decomposed by the contact and one by the chemical action; if the ratio be as 2 : 1, the decomposition will have taken place in equal proportions between the two. All the phenomena are perfectly consistent with this view. As a fact, we know that the contact action proceeds far more rapidly at a high than at a low temperature; we need not therefore be surprised if the relative velocity of this to the chemical action

* I have made the experiment of heating the dry peroxide with oxide of silver until the latter was reduced, but the loss of oxygen was only that of the silver. It is however remarkable, that when it is heated in a similar manner with chloride of silver, the chloride is reduced and the two equivalents of oxygen of the peroxide evolved. This decomposition takes place also with baryta, but not with lime; and I cannot but suspect that it is connected with the peculiar property of baryta of taking up a second equivalent of oxygen which does not belong to lime. It is moreover extremely difficult to prepare a baryta quite free from peroxide and water, so as to make a truly comparative experiment.

increases with the temperature. By increasing the mass of the oxide or chloride, on the other hand, the velocity of the chemical action is relatively increased ; in this case therefore we have a great reduction. Again, a substance in a fine state of division is decomposed more rapidly than one which is dense and compact; here, therefore, and in other similar differences, is the cause of the different results given by different preparations of the peroxide*.

By the words *contact* and *chemical*, I mean to express no theory, and am indeed drawing but a momentary distinction between facts, for I cannot believe that the one of these portions of oxygen is formed according to one law and the other in a different manner, that the one fact is a chemical synthesis and the other not. The only difference between them I believe to be, that in the case of the action I have called chemical, the peroxide of barium decomposes peroxide of lead, or oxide of silver, or the like; and in the contact action one particle of peroxide of barium decomposes another particle of the same substance, the platinum, silver oxide or other body causing that chemical relation between the particles which renders the decomposition possible. The important question as to the nature of that definite relation which these experiments indicate between the contact action and the chemical action, I reserve for future inquiry.

I have made various experiments to ascertain whether the same kind of reduction could be effected by means of other metallic peroxides, such, for example, as the peroxide of lead or manganese, as with the peroxide of barium and potassium, but without success. I believe this to admit of a very rational explanation, and that this reducing power is a result of the peculiar chemical nature of the alkaline metals and their compounds; in short, of what is usually termed their powerful chemical affinities and position on the electro-chemical scale, to which indeed we may distinctly trace it. This relation may be expressed in various ways, but which mean essentially one and the same thing. If, for example, in the last experiment we express the change which takes place thus—

$$\underbrace{\overset{+}{\mathrm{Ba}}\,\overset{-}{\mathrm{O}}\,\overset{+}{\mathrm{O}}\,\overset{-}{\mathrm{O}}\,\overset{+}{\mathrm{H}}}\,\overset{-}{\mathrm{I}}=\mathrm{Ba\,I}+\mathrm{O}_2+\mathrm{HO},$$

it follows, from the view I have given of the mutual relation of these particles, and the interdependence of these chemical changes, that we cannot substitute for the barium a metal which stands in a different chemical relation to the particles between which it is placed without altering the relation of all the other particles of the system, so that if the chemical difference on which combination depends does not exist between the metal and the iodine, neither can it exist between the particles of the oxygen. In this way the fact, at first sight very anomalous, admits of a very simple explanation,

* I by no means wish to exclude from these a real chemical difference in their nature, which the behaviour of certain analogous bodies leads me to suspect.

that the peroxide of barium, the less reducible peroxide, is that which under these circumstances is thus readily decomposed.

Lastly, let me observe, that I have limited my assertions as to the nature of the elemental bodies, to the statement, that, under certain conditions, there exists a chemical difference between the particles of which they consist. On the chemical nature of these particles I have offered no opinion. The apparent and obvious inference from the experiments is doubtless that the elements form a peculiar group of chemical substances, consisting of similar particles or atoms in a state of combination, as other bodies consist of dissimilar. Of this view, in the early part of this paper, I have already spoken; it is the hypothesis of AMPÈRE. Many theoretical difficulties however meet us, when we come logically and consistently to carry out this idea to the explanation of chemical phenomena, especially to the phenomena of direct combination and to the simplest cases of chemical decomposition; and it by no means follows that, although the apparent, it is the rational and philosophical interpretation of the experiments. Besides this view and that of BERZELIUS, there is yet a third hypothesis which we may form as to the constitution of these elements, namely, that they consist of yet other and further elements. On this view, the real fact which lay hid under these phenomena, might be the synthesis of the oxygen from the ultimate and further elements of which the oxygen consisted. In the present state of our knowledge it is useless to dilate on this idea; but on the assumption that the elemental bodies are in this sense compound, we may, I believe, account for all these experiments without ever assuming a chemical difference between two similar particles; and it appears to me perfectly possible, that in such a constitution of the elemental bodies, these experiments, together with the phenomena of allotropy, may find their ultimate solution.